

SHOSTAKOVSKIY, M.F.

Ionic polymerization of vinyl ethers. M. F. Shostakov\*,  
Bil. I. Mikhail'ev, and N. N. Ovchinnikova (Inst.  
Org. Chem. Acad. Sci. U.S.S.R., Moscow). Izvest. Akad.  
Nauk S.S.R., Oddel. Khim. Nauk, 1953, 1056-60; cf.  
C.A. 48, 12062c.—ROCH<sub>2</sub>CH<sub>2</sub> were polymerized by treat-  
ment with a trace of 5% FeCl<sub>3</sub>·6H<sub>2</sub>O in BuOH (vigorous re-  
action). The polymers, which were sol. in the usual org.  
solvents, had the following properties (% yield,  $\eta_{sp}^{\text{DCC}}$ ,  
and mol. wt., resp., given): (As shown): *Et*, 68, 0.9123,  
1.4644, 2545; *iBu*, 70, 0.9576, 1.4520, 5334; *Pr*, 90, 0.9368,  
1.4528, 4850; *iso-iBu*, 61, 0.9263, 1.4520, 4580; *Bu*, 92,  
0.9290, 1.4570, 4758; *iso-Bu*, 90, 0.9205, 1.4505, 4183;  
*iso-1-3*, 86, 0.9117, 1.4607, 4048; *C<sub>7</sub>H<sub>14</sub>*, 89, 0.9120, 1.4632,  
4003; *cyclohexyl*, 92, 0.9364, 1.4894, 1645; *C<sub>7</sub>H<sub>16</sub>*,  
0.9132, 1.4651, 3009; *C<sub>9</sub>H<sub>16</sub>*, 89, 0.9230, 1.4667, 4202;  
*isobutyl*, 93, 0.9307, 1.4661, 3261; *C<sub>9</sub>H<sub>16</sub>*, 87, 0.9118  
1.4670, 3799; *C<sub>10</sub>H<sub>22</sub>*, 80, 0.9282, 1.4682, 5138.

G. M. Kosolapoff

LFH

SHOSTAKOVSKIY, M.F.

✓ Derivatives of unsaturated tertiary alcohols. I. Synthesis of acetylenic acetals based on vinyl ethers and acetylenic alcohols. M. F. Shostakovskii and I. A. Shikhiev (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.R., Otdel. Khim. Nauk* 1953, 1061-7. To 42 g.  $\text{Me}_2\text{C}(\text{OH})\text{C}\equiv\text{CH}$  and 72 g.  $\text{EtOCH}=\text{CH}_2$  (which failed to react alone) was added 0.02 ml. 30% HCl and the mixt. allowed to stand overnight; distn. after drying with  $\text{K}_2\text{CO}_3$  gave 79.5%  $\text{MeCH(OEt)OCMe}_2\text{C}\equiv\text{CH}$ ,  $b_{11-12} 42-3^\circ$ ,  $d_{40}^{20} 0.8701$ ,  $n_D^{20} 1.4102$ , readily hydrolyzing in 2%  $\text{H}_2\text{SO}_4$  to  $\text{Me}_2\text{C}(\text{OH})\text{C}\equiv\text{CH}_2$  (I),  $b_1 70-82^\circ$ ,  $d_{40} 0.8976$ ,  $n_D^{20} 1.4468$ . Similarly iso- $\text{PrOCH}=\text{CH}_2$  gave 76.5%  $\text{MeCH(OCHMe}_2)_2\text{C}\equiv\text{CH}_2$ ,  $b_{10-11} 153-5^\circ$ ,  $b_{11-12} 47-8^\circ$ ,  $d_{40} 0.8568$ ,  $n_D^{20} 1.4150$ . Heating this acetal (42.6 g.) with 42 g.  $\text{MeC}(\text{OH})\text{C}\equiv\text{CH}$  in a sealed tube 52 hrs. at 170-80° gave a little iso- $\text{PrOH}$ , 20.7 g.  $\text{Me}_2\text{C}(\text{OH})\text{C}\equiv\text{CH}$  and 43.4 g. crude (32% pure) I,  $b_1 74-8^\circ$ ,  $d_{40}^{20} 0.8967$ ,  $n_D^{20} 1.4412$ . iso- $\text{BuOCH}=\text{CH}_2$  similarly gave 78.2%  $\text{MeCH(OCH}_2\text{CHMe}_2)_2\text{C}\equiv\text{CH}_2$ ,  $b_{10} 173-4^\circ$ ,  $b_{11-12} 56-6^\circ$ ,  $d_{40} 0.8887$ ,  $n_D^{20} 1.4170$ . BuOCH $=\text{CH}_2$  similarly gave 81.5%  $\text{MeCH(OBu)}_2\text{C}\equiv\text{CH}_2$ ,  $b_{10} 181-2^\circ$ ,  $b_{11-12} 62-3^\circ$ ,  $n_D^{20} 1.4182$ ,  $d_{40} 0.8592$ . The Bu and iso-Bu derivs. were most stable thermally in respect to disproportionation.

G. M. Kosolapoff

1. SHOSTAKOVSKIY, V. F., SIDEKOVSAYA, F. P.
2. USSR (600)
4. Lactams
7. Activation of vinylcaprolactam in the presence of hydrogen peroxide. Izv. AN SSSR, Otd. khim. nauk. no. 1, 1953
9. Monthly List of Russian Accessions, Library of Congress, June 1953. Unclassified.

SHOSTAKOVICH, M. Ye.; GRACHIEV, N. A.; VOLKOVA, Z. S.

Glycols

Transformations of vinyl ethers. Part 8. Transformations of ethylene glycol acetals  
Izv. AN SSSR. Otd. khim. nauk. No. 1, 1953.

Monthly List of Russian Accessions, Library of Congress, June 1953. Uncl.

SHOSTAKOVSKI, M. F.

6  
Comparison of the action of metallic chlorides on polymerisation.  
Catalysis of polymerisation of styrene by ferric and stannic chlorides. M. F. Shostakovskii and V. A. Gladyshevskaya [Izvestia, 1953, No. 2, 351-356]. In the presence of  $FeCl_3 \cdot 6H_2O$ , styrene does not polymerise in  $N_2$ , and forms polystyrene and benzaldehyde in air, whereas in presence of  $SnCl_4$  it polymerises in both  $N_2$  and air.  
R. C. MURRAY.

SHOSTAKOVSKIY, M.F.; PRILEZHAYEVA, Ye.N.; SHAPIRO, Ye.S.

Synthesis of sulfur compounds based on vinyl ethers and acetylene. Part  
6. Reaction of mercaptans with vinyl ethers. Izv. AN SSSR. Otd.khim.  
nauk. no.2:357-367 Mr-Ap '53. (MLRA 6:5)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(Mercaptans) (Vinyl ethers)

SHOSTAKOVSKIY, M.F.; CHEKULAYEVA, I.A.

Synthesis and transformations of vinyl ethers of ethanolamines. Part 3.  
Nature of the double bond of vinyl ethers of ethanolamines. Izv. AN SSSR.  
Otd.khim.nauk. no.2:368-373 Mr-Ap '53. (MIRA 6:5)

1. Institut organicheskoy khimii Akademii nauk SSSR. (Vinyl ethanolamine)

*synthesis of mixed ethers and polyethers of polyatomic alcohols.* A. P. Melchitsyakov, M. P. Slobodkovskii, and P. V. Tsvetov (Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow). *Sbornik Statei Oshchchi Khim.* 2, 824-30 (1953).—Hydrogenation of alkyl vinyl ethers over Bag Al-Ni alloy catalyst (cf. *C.A.* 31, 1000\*) readily yields the corresponding mixed ethers. The catalyst is prepd. by treatment of 150 g. 50% Al-Ni alloy with 500 ml. 4% NaOH, then with a similar amt. of NaOII after subsidence of the reaction, and 2 more similar aunts. after 3-4 hrs. The catalyst retains appreciable amts. of Al, thus differing from the conventional Raney Ni. The hydrogenations were run at 80-140 atm. II and gave about 95% yields of the satd. ethers. Thus,  $\text{BuOCH:CH}_2$  gave  $\text{EtOBu}$ ;  $(\text{CH}_3\text{OCH:CH}_2)_2$  gave  $(\text{CH}_3\text{OEt})_2$ , b. 165-5.5°,  $d_{4}^{20}$  0.8420,  $n_{D}^{20}$  1.4030. G. M. Kosolapoff

SHOSTAKOVSKIY, M. F.

~~CZECH~~

Synthesis and transformations of vinyl aryl ethers. III.  
Synthesis of aralkyl and diaryl acetals. M. F. Shostakovskii,  
A. V. Kalubina, and A. D. Dariev (Stavropol Univ., Irkutsk),  
*Sbornik Statei Obozrechenii Khimi*, 2, 1297-1301 (1959).  
cf., *Zh.* 42, 7243; 43, 3272a.—Treatment of mixts. of *p*-  
 $\text{Me}_2\text{CC}_6\text{H}_4\text{OCH}_2\text{CH}_3$  and alkyl vinyl ether with a little HCl yielded  
mixts. which on distn. gave 51-76% yields of the correspond-  
ing mixed acetal and low yields of the sym. diaryl acetal;  
the same products were obtained on heating the phenol with  
 $\text{p-Me}_2\text{CC}_6\text{H}_4\text{OCH}_2\text{CH}_3$  in an autoclave 12 hrs. at 220-5°.  
The following  $\text{MeCH}(\text{OR})\text{OC}_6\text{H}_4\text{CMc}_2-p$  ( $\text{R} = \text{b}, \text{o}, \text{m}$ ,  
 $n^2_0$ , dig given) were reported:  $\text{Me}$ , 72-3°/4, 1.4620, 0.9600;  
 $\text{Et}$ , 127-8°/4, 1.4875, 0.9620;  $\text{Pr}$ , 85-6°/2, 1.4820, 0.9363;  
 $\text{Bu}$ , 155-6°/10, 1.4850, 0.9343;  $\text{Bu}_2$ , 125-6°/4, 1.4705,  
0.9317;  $\text{Am}$ , 122-3°/2, 1.4810, 0.9257;  $\text{Ph}$ , 145-7°/3,  
1.5370, 1.0283;  $\text{MeCH}(\text{OCH}_2\text{CH}_3\text{CMc}-p)_2$ , 151-2°/3,  $n^2_0$  1.5110,  
 $d_{40}^2$  0.9446. *G. M. Kosolapoff*

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gave*

SHOSTAKOVSKIY, M.F.; MIKHANT'YEV, B.I.; OVCHINNIKOVA, N.N.

Indirect vinylation of monocarbonic acids and oxyacids. Izv.AN SSSR Otd.  
khim.nauk no.3:556-561 My-Je '53. (MLRA 6:8)

1. Institut organicheskoy khimii Akademii nauk SSSR.

(Esters)

SHOSTAKOVSKIY, M.F.; GERSHTEYN, N.A.

Conversations of vinyl ethers. Chemical properties of alkyl- $\beta$ -chloroethyl-acetals. Izv. AN SSSR. Otd. khim. nauk no. 4:716-720 Jl-Ag '53. (MLRA 6:8)

1. Institut organicheskoy khimii akademii nauk SSSR. (Vinyl compounds)

SHOSTAKOVSKIY, M.F.; MIKHANT'YEV, B.I.; OVCHINNIKOVA, N.N.

Ionic copolymerization of vinyl ethers. Izv. AN SSSR. Otd. khim. nauk no. 4:  
721-725 Jl-Ag '53. (MLRA 6:8)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(Polymers and polymerization) (Vinyl ethers)

SHOSTAKOVSKIY, M. S.

USSR/ Chemistry - Synthesis

Card 1/1 : Pub. 40 - 20/22

Authors : Shostakovskiy, M. S.; Shikhiev, I. A.; and Kochkin, D. A.

Title : Synthesis and conversions of oxygen-containing silicon-organic compounds. Part 1.- Synthesis of silicon-organic acetals

Periodical : Izv. AN SSSR. Otd. khim. nauk 5, 941-944, Sep-Oct 1953

Abstract : A new synthesis of O-containing silicon-organic compounds, based on the reaction of vinyl ethers and silanols, is discussed. It was established for the first time that triethylsilanol condenses with vinylbutyl and vinylisobutyl ethers in conditions analogous to corresponding syntheses with organic alcohols. The synthesis of hitherto unknown nonsymmetrical butyl- and isobutyltriethylsilaneacetals, is described. A new method for the derivation of various silicon-organic acetals, is presented. Three USSR references (1933-1952).

Institution : Academy of Sciences, Institute of Organic Chemistry

Submitted : December 23, 1952

SHOSTAKOVSKIY, M.F.; SHIKHIYEV, I.A.; KOCHKIN, D.A.

Investigation in the field of synthesis and conversions of silicon organic compounds containing oxygen. Report no.1: Synthesis of silicon-organic acetals. Izv.AN SSSR Otd.khim.nauk no.5:941-944 S-0 '53. (MLRA 6:10)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(Acetals) (Silicon organic compounds)

SHOSTAKOVSKIY, M.F.; KHOMUTOV, A.M.

Research in the field of chemical conversions of unsaturated and high molecular weight compounds. Report no.1. Copolymerization of methacrylic acid and vinylalkyl ethers. Izv.AN SSSR. Otd.khim.nauk no.6: 1048-1055 N-D '53. (MLRA 6:12)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(High molecular weight compounds) (Methacrylic acid) (Ethers)

SHOSTAKOVSKIY, M.F.; MIKHANT'YEV, B.I.; OVCHINNIKOVA, N.N.

Ionic polymerization of vinyl ethers. Izv.AN SSSR. Otd.khim.nauk no.6:  
1056-1060 N-D '53. (MLRA 6:12)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(Vinyl ethers) (Polymers and polymerization)

SHOSTAKOVSKIY, M.F.; SHIKHIYEV, I.A.

Research in the field of the derivatives of tertiary unsaturated alcohols. Report no.1. Synthesis of acetylene acetals based on vinyl ethers and acetylene alcohols. Izv. AN SSSR, Otd. khim. nauk no.6:1061-1067 N-D '53. (MLRA 6:12)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(Acetals) (Acetylene derivatives) (Ethers)

SHOSTAKOVSKY, M. F.

Analytical Abst.  
Vol. 1 No. 2  
Feb. 1954  
Organic Analysis

(S) Chem

306. Methods of analysis of halogenated ethers.  
I. Analysis of  $\alpha$ -halogen-dialkyl and ethylaryl ethers. M. F. Shostakovskiy and A. V. Bogdanova. (*J. Anal. Chem., U.S.S.R.*, 1953, 8 [4], 231-234).— Compounds of the type  $RCH_2CHXOR'$  where  $R = H$  or  $CH_3$ ,  $X = Cl$  or  $Br$ , and  $R' = Alkyl$  or  $Aryl$  are hydrolysed instantaneously at room temp. to  $RCH_2CHO$ ,  $HX$  and  $R'OH$  by excess of water. Detection of the compounds can be based on tests for aldehyde, halide, or acid. They can be determined by hydrolysis followed by titration with 0.1 N NaOH, titration with 0.1 N  $AgNO_3$ , or titration of the aldehyde with bisulphite. A number of different compounds were determined in this way with excellent results. G. S. SMITH.

MF  
2-21

SHOSTAKOVSKY, H. F.

Chem Abs  
148 25 Jan 54

Organic Chem

Decomposition of benzoyl peroxide in the medium of some vinyl compounds. M. F. Shostakovskii, E. P. Gracheva, and V. A. Neterman. *Zhur. Obshchey Khim.* 23, 51-60 (1953).—Bz<sub>2</sub>O<sub>2</sub> (12 g.) in 72.1 g. CH<sub>2</sub>:CHOAc and 120 g. petr. ether heated to 80-7.5° in N atm. over 5 hrs. gave 0.7480 g. O, 0.0384 g. CO<sub>2</sub>, and 0.0366 g. H<sub>2</sub>O, with 94.33% decompr. leading to O formation. The secondary source of CO<sub>2</sub> appears to be destructive oxidation of CH<sub>2</sub>:CHOAc. Similar reaction in the presence of CH<sub>2</sub>:CMe-CO<sub>2</sub>Me gave 0.4043 g. O, 0.0171 g. CO<sub>2</sub>, and 0.0542 g. H<sub>2</sub>O, while the reaction in the presence of PhCH:CH<sub>2</sub> gave 0.0738 g. CO<sub>2</sub>. The reaction in the presence of CH<sub>2</sub>:CHOAc gave some BzOH, polyvinyl acetate, AcOH, and AcH. With CH<sub>2</sub>:CMeCO<sub>2</sub>Me the by-products included polymethyl methacrylate, while the reaction in the presence of PhCH:CH<sub>2</sub> run similarly at 88° gave only 3.38% decompn. of the peroxide to CO<sub>2</sub>. Heating 100 g. BuOCH:CH<sub>2</sub> and 12 g. Bz<sub>2</sub>O<sub>2</sub> 38 hrs. gave 97.7 g. unchanged BuOCH:CH<sub>2</sub> and 4.7 g. product, bp 74-5°, n<sub>D</sub><sup>20</sup> 1.4040, d<sub>4</sub> 0.8260, and 13.1 g. viscous solid, besides 3.75 g. BzOH. The distd. product analyzed as C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>. Thus peroxides like Bz<sub>2</sub>O<sub>2</sub> serve as supply of both free radicals and O, the latter being able to serve as a chain initiator in polymerization reactions of vinyl deriv. present in the system. Vinyl ethers are not polymerized by these means as they are not polymerized by atm. O. G. M. Kosolapoff

SHOSTAKOVSKIY, M.F.

Acetylenic alcohols and glycols. I. Synthesis and  
transformations of 1,4-butyndiol. M. F. Shostakovskii  
and A. V. Bogdannova. *J. Gen. Chem. U.S.S.R.* 23, 67-81  
(1953) (Engl. translation).—See C.A. 48, 12416.  
H. L. H.

SHOSTAKOVSKIY, M.F.; GRACHEVA, Ye.P.

Investigation in the field of synthesis and conversions of substituted  
vinyl ethers. Part 1. Synthesis of  $\alpha$ -substituted vinyl ethers. Zhur. ob.  
khim. 23 no.7:1153-1158 Jl '53. (MLRA 6:7)

1. Institut organicheskoy khimii Akademii Nauk SSSR, Laboratoriya vini-  
lovykh efirov. (Ethers) (Vinyl derivatives)

SHOSTAKOVSKIY, M.F.; MIKHANT'YEV, B.I.; OVCHINNIKOVA, N.N.; NETERMAN, V.A.

Synthesis of incomplete acylals of lactic acid. Zhur. ob. khim. 23 no.7:  
1167-1173 Ju '53. (MILRA 6:7)

1. Institut organicheskoy khimii Akademii Nauk SSSR.  
(Lactic acid) (Ethers)

SUBSTANCE, U. S.

4

*Synthesis and transformations of  $\alpha$ -methylvinyl butyl ether.* II. M. F. Shostakovskii and B. P. Gracheva.  
Zhur. Obschhei Khim. 23, 1320-3 (1953); cf. C.A. 47,  
12217c.—Heating 111 g. BuOH, 50 g. Me<sub>2</sub>CH, and 10 g.  
powd. KOH in an autoclave 14 hrs. at 248-50° (58 atm.  
max. pressure) gave 75.8% CH<sub>2</sub>CMeOBu, b<sub>4</sub> 111-12°,  
 $n_{D}^{20}$  1.4111, d<sub>4</sub> 0.7955. When shaken 1 hr. with 1% H<sub>2</sub>SO<sub>4</sub>,  
it is completely hydrolyzed, yielding Me<sub>2</sub>CO. The ether  
(11.4 g.) and 7.4 g. BuOH stirred 30-40 min. and treated  
with 2 drops concd. HCl reacted exothermically and distn.  
of the mixture gave 81% Me<sub>2</sub>C(OBu)<sub>2</sub>, b<sub>4</sub> 70°,  $n_{D}^{20}$  1.4150,  
d<sub>4</sub> 0.8303. This is completely hydrolyzed by shaking 1 hr.  
with 1% H<sub>2</sub>SO<sub>4</sub>, yielding Me<sub>2</sub>CO. G. M. Kosolapoff

SHOSTAKOVSKIY, M. F.

USSR

Azeotropic mixtures of vinyl alkyl ethers with alcohols.  
II. M. F. Shostakovskii, E. N. Prilezheva, and N. I. Uvarova. *J. Appl. Chem. U.S.S.R.* 26, 1003-8 (1953)  
(Engl. translation). See C.A. 48, 10534d. H. L. H.

SHOSTAKOVSKIY, M.F.; PRILEZHAYEVA, Ye.N.; UVAROVA, N.I.

Azeotropic mixtures of vinylalkyl ethers and alcohols. Zhur.prikl.khim. 26  
no.10:1074-1079 O '53. (MLRA 6:10)

1. Institut organicheskoy khimii Akademii nauk SSSR. Laboratoriya vinilovykh  
soyedineniy. (Azeotropy) (Vinyl ethers) (Alcohols)

SHOSTAKOVSKIY, M. F.

Chemical Abst.  
Vol. 48  
Apr. 10, 1954  
Organic Chemistry

Optical study of the hydrogen bond in some mono- and polyglycols. M. P. Shostakovskii, M. I. Batuev, P. V. Tyupacev, and A. D. Matveeva. *Doklady Akad. Nauk S.S.R.*, 89, 601-4 (1953).—The Raman spectra of mono- and vi-ethers of glycol,  $\text{CH}_2(\text{CH}_2\text{OH})_n$ ,  $\text{O}(\text{CH}_2\text{CH}_2\text{OH})_n$ , and  $(\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})_n$  show a long-wave displacement of the OH frequency with typical smearing of the band at 3200-3000 cm<sup>-1</sup>. Cryoscopic mol. wts. also show assoc. increasing with increased concn. of the ethers in  $\text{C}_6\text{H}_6$ , the isomeric cyclic acetals of glycol,  $\text{CH}_2(\text{CH}_2\text{OH})_2$ , and  $(\text{CH}_2\text{CH}_2\text{OH})_2$ , which cannot form H bonds also show lower b.p.s. and lower viscosities than are shown by their isomers: vinyl glycol ethers. The latter show isomerization into the acetals in solns. in  $\text{CCl}_4$ ; this does not occur in  $\text{C}_6\text{H}_6$ . G. M. Kosolapoff

SHOSTAKOVSKIY, M. F. - BATUEV, M. I. - TIUPAEV, P. V. - MATVEYEVA, A. D.

Oxonium

Oxonium theory and its optical substantiation on simple vinyl ethers.  
Dokl. AN SSSR 89 no. 1, 1953

9. Monthly List of Russian Accessions, Library of Congress, May 1953. Unclassified.

SHOSTAKOVSKIY, M.-F.

Synthesis and transformations of oxygen-containing  
silicoorganic compounds. Synthesis of methyl, ethyl, and  
isopropyl triethylsilane acetals. M. F. Shostakovskii, K. A.  
Andrianov, I. A. Slukhiey, and D. A. Kochkin. *Doklady  
Akad. Nauk S.S.R.* 93, 681-3 (1953); cf. preceding abstr.  
—Heating 33 g. Et<sub>3</sub>SiOH, 19 g. MeOCH<sub>2</sub>CH<sub>3</sub> and 0.02 ml.  
30% HCl in sealed tube 6.5 hrs. at 65° gave 58.0% Me-  
CH(OEt)OSiEt<sub>3</sub>, b.p. 74-5°, n<sub>D</sub><sup>20</sup> 1.4235, d<sub>20</sub> 0.8726. To 33 g.  
Et<sub>3</sub>SiOH and 30 g. EtOCH<sub>2</sub>CH<sub>3</sub> was added 0.02 ml. 30%  
HCl and the mixt. was heated 1 hr. to 50° and left overnight;  
after drying it gave 45.1% MeCH(OEt)OSiEt<sub>3</sub>, b.p. 78-9°,  
n<sub>D</sub><sup>20</sup> 1.4232, d<sub>20</sub> 0.8682. Similarly iso-PrOCH<sub>2</sub>CH<sub>3</sub> and Et<sub>3</sub>  
SiOH with 30% HCl catalyst gave after 8.5 hrs. in a sealed  
tube at 65° gave 42% MeCH(OCHMe<sub>2</sub>)OSiEt<sub>3</sub>, b.p. 87-9°,  
d<sub>20</sub> 0.8561, n<sub>D</sub><sup>20</sup> 1.4238. G. M. Kosolapoff.

SHOSTAKOVSKIY, M. I.

U.S.S.R.

Synthesis and transformations of unsaturated organo-silicon compounds. I. Synthesis of vinylsilane chlorides by a direct method. M. F. Shostakovskii and D. A. Koskin. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1954, 145-6 (Engl. translation).—See C.A. 49, 6090b.  
H. L. H.

SHOSTAKOVSKIY, M. F.

S S R .

✓ Stabilization of  $\alpha$ -nitrogenated ethers. M. F. Shostakovskii and A. V. Bogaturova (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). Izvest. Akad. Nauk S.S.R., Otdel. Khim. Nauk 1954, 102-5.—Satisfactory stabilization for several months or years of  $\text{EtOCH(MeCl)}$ ,  $\text{EtOCH(MeBr)}$ , and  $\text{BuOCH(MeBr)}$  is attained by addition to them of 15-20%  $\text{Et}_2\text{O}$ . For stabilization at elevated temp. (2 months at  $60^\circ$ ) the amt. of added  $\text{Et}_2\text{O}$  must be about 50%. Dioxane is less effective, as is  $\text{CaH}_2$ , although both show some protective action. G. M. Kosolapoff

SHOSTAKOVSKIY, M. F.

USSR

Reaction of vinyl and polyfunctional compounds. I. Reaction of vinyl alkyl ethers with glycerol. M. F. Shostakovskii, V. V. Zhebrovskii, and M. A. Medelyanovskaya (Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow). Izv. Akad. Nauk S.S.R. Otdel. Khim. Nauk 1954, 168-72; Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1954, 137-41 (English translation).—Stirring 14.4 g.  $\text{EtOCH}_2\text{CH}_2$  and 18.4 g. glycerol 0.5 hr. and adding 1 drop HCl catalyst gave an exothermic reaction (temp. rise to 70.5°), after which the mixt. was neutralized and distd., yielding 7.5 g. mixed  $\text{EtCH}_2$  and  $\text{MeCH}(\text{OEt})_2$ , and 17.8 g. crude product, bp 70-93°, which could not be resolved into pure components. This with  $\text{BzCl}$  in pyridine gave 5.9 g. solid benzoate (I) and 11.36 g. liquid benzoate (II); I was identified as 1,3-ethyleneglycerol benzoate, m. 85°, and II as the 1,2-ethyleneglycol isomer,  $\text{bp}_{10}\text{-}101.2^\circ$ ,  $\text{d}_{4}^{20} 1.1558$ ,  $n_{D}^{20} 1.5140$ . I heated with 10% KOH until a clear soln. formed and the cooled soln. satd. with  $\text{LiCO}_3$  and extd. with  $\text{Et}_2\text{O}$  yielded 35% 1,3-ethyleneglycerol,  $\text{bp}_{10}\text{-}65-8^\circ$ ,  $n_{D}^{20} 1.4520$ ,  $n_{D}^{20} 1.4538$ . II similarly gave 43% 1,2-ethyleneglycerol,  $\text{bp}_{10}\text{-}84-5^\circ$ ,  $n_{D}^{20} 1.4436$ .  $\text{EtOCH}_2\text{CH}_2$  (3 moles) treated with 1 mole glycerol did not form these derivs.; the products were  $\text{EtOH}$ ,  $\text{MeCH}(\text{OEt})_2$ , and bis(ethyleneglycerol). To 25.04 g.  $\text{BuOCH}_2\text{CH}_2$  and 23 g. glycerol was added 3 drops HCl catalyst and the mixt. heated 0.5 hr. to 50°, at which point an exothermic reaction took place; after neutralization the mixt. yielded 11.87 g.  $\text{BuOH}$  and 23 g. crude product,  $\text{bp}_{10}\text{-}85-103^\circ$ , which, benzyloylated as above, yielded 9.3 g.  $\text{BuOBz}$  and 29.98 g. II; no I was found. It is believed that the reaction proceeds through formation of mixed acetals with subsequent cyclization to the final products.  
G. M. Kosolapoff

SHOSTAKOVSKIY, M. F.

USSR.

✓ Synthesis and transformations of unsaturated ~~organo~~ <sup>organo</sup> silicon compounds. I. Synthesis of vinylsilane chlorides by a direct method. M. F. Shostakovskii and D. A. Kozhukhin (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). Izvest. Akad. Nauk S.S.R., Otdel. Khim. Nauk, 1954, 174-5.—An Fe pipe (60 mm. by 100 cm.) was charged with 1.5 kg. 20/80 Cu-Si alloy in 10-15 mm. pieces, heated to 380-400° 50 min. in a dry N stream for drying, and CH<sub>2</sub>-CHCl passed in at 0.1 l./min. because of uneven temp. Distribution, coke formation developed in parts of the tube; after 80 hrs. there was collected 750 g. product, which on fractionation yielded 29.3% CH<sub>2</sub>-CHSiCl<sub>3</sub>, b<sub>100</sub> 92.5-4.0°, d<sub>40</sub> 1.2050, and about 9% (CH<sub>2</sub>-CH)<sub>2</sub>SiCl<sub>3</sub>, b<sub>100</sub> 118-19°, d<sub>40</sub> 1.0813.  
G. M. Kosolapov

**SHOSTAKOVSKII, M.F.**

Syntheses of sulfur compounds from vinyl ethers and acetylenes. VII. Peculiarities of the addition of Markovnikov-hydrogen sulfide to vinyl butyl ether against the Markovnikov rule. N. N. Shcherbakov, E. N. Priluzhnev, and G. S. Shadrin. (N. I. Zelinskii Inst. Org. Chem., Acad. SSSR, Moscow.) Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1954, 202-2023; cf. C. A., 46, 9311.—Addition of  $H_2S$  to  $\text{BuOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  is catalyzed by small amounts of  $\text{O}_2$ , which leads to contra-Markovnikov order of addition, ascertainable by titration with  $\text{AgNO}_3$ . Antioxidants do not cause peroxidation also give this result.

Antioxidants also give this result. Larger hinder the reaction thus proving its radical nature. Larger amounts of  $\text{O}_2$ ,  $\text{Br}_2$ , and  $\text{H}_2\text{O}_2$  inhibit the reaction, probably by chain breaking through oxidation of chain-leading radicals.

Heating 1 mole  $\text{BuOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ , with 1.5 mole  $\text{RSCH}_2$  ( $\text{RC}\equiv\text{CH}_2$ ) in the cold yields  $\text{BuOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$ . But in the cold yields  $\text{BuOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_3$ .

$\text{BuOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  stored for a long time over  $\text{Na}$  and showing a quinonoid tint, but  $\text{BuOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  stored over  $\text{KCO}$  reacts very sluggishly. A good catalytic effect is produced by addition of  $\text{HgCl}_2$  in dioxane.

General method of synthesis of  $\beta$ -alkoxymethylmercaptoalkanes.

Reaction of  $\text{H}_2S$  and  $\text{ROCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  in  $\text{CHCl}_3$  (ref. 103-13) — reaction of  $\text{O}_2$  yields the corresponding alkoxylates. In the presence of  $\text{O}_2$  yields the corresponding sulfides, predominantly in ethylcyclohexane and corresponding sulfides, predominantly in cyclohexanone, contra-Markovnikov structure, especially noted in branched ethers, tend to give the normal addition products.

Keeping 15 g.  $\text{BuOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and 0.05 g.  $\text{HgCl}_2$  in  $\text{CHCl}_3$  for 10 days gave 58.10%  $\text{BuOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$ , sealed tube 1 h. 1.4350, d<sub>4</sub><sup>20</sup> 0.912, and 5.1 g.  $(\text{BuOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{S}$ , n<sub>D</sub><sup>20</sup> 1.45-1.47,  $d_{4}^{20}$  0.915-0.917, and a mixture of  $(\text{BuOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{S}$  and  $\text{HgS}$  yielded 5.9%  $(\text{BuOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{S}$ , n<sub>D</sub><sup>20</sup> 1.4778, d<sub>4</sub><sup>20</sup> 0.9227, and a mixture of  $(\text{BuOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{S}$  and  $\text{HgS}(\text{O}_2\text{P})_2$ , b.p. 130-135°, containing 50% of the latter observed by titration. In this mixture, the latter was  $\text{HgS}(\text{O}_2\text{P})_2$ , gave the pure former sulfide, b.p. 135-136°,  $n_{D}^{20}$  1.4516,  $d_{4}^{20}$  0.9155. The reaction of  $\text{HgS}(\text{O}_2\text{P})_2$  with  $\text{HgCl}_2$  gave the pure  $\text{HgS}$ , b.p. 135-136°,  $n_{D}^{20}$  1.4516,  $d_{4}^{20}$  0.9155.



SHOSTAKOVSKY, M. F.

USSR

Some reactions which proceed during the processes of  
polymerization of vinyl butyl ether. M. F. Shostakovskiy  
and V. A. Gladyshevskaya. Bull. Acad. Sci. U.S.S.R.,  
Div. Chem. Sci. 1954, 299-304 (Engl. translation). See  
C.A. 49, 4508a. H. L. H. ① *W*

SHOSTAKOVSKIY, M.F.

USSR

✓ Synthesis and transformations of vinyl ethers of ethanolamines. IV. Copolymerization of vinyl ether of 2-aminoethanol and methyl ester of methacrylic acid. M. F. Shostakovskii, I. A. Chekulayeva, and A. M. Kholmutov (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). Izvest. Akad. Nauk S.S.R., Otdel. Khim. Nauk 1954, 323-8; cf. C.A. 48, 5794t.—Pure  $\text{CH}_2\text{:CHO-CH}_2\text{CH}_2\text{NH}_2$  does not polymerize under action of  $\text{Bz}_2\text{O}_2$  in 100 hrs. at 60°. In mixts. with Me methacrylate it copolymerizes in varying proportions, yielding products contg. 0.25-5.3% N; the copolymers with appreciable amt. of N are generally insol. and infusible. No polymer of Me methacrylate usually forms in the course of copolymerization, but the yields of the copolymer are usually quite low. Expts. with copolymerization yielded varying amts. of  $\text{CH}_2\text{:CHOCH}_2\text{CH}_2\text{NHCH}_2\text{CHMeCO}_2\text{Me}$ ,  $n_D^{20} 1.4491$ ,  $d_4^{\text{25}} 0.9998$ , which hydrogenated over Raney Ni to the satd. analog,  $n_D^{20} 1.4333$ ,  $d_4^{\text{25}} 0.9608$ .  
G. M. Kosolapoff

SHOSTAKOVSKY, M.F.

USSR:

✓ Some reactions which proceed during the polymerization of vinyl butyl ether. M. F. Shostakovskiy and V. A. Gladyshevskaya (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.R., Otdel. Khim. Nauk* 1954, 362-9. — Heating 100 g. of a mixt. of 93% BuOCH<sub>2</sub>CH<sub>3</sub> and 8% BuOH with 0.24 g. 5% FeCl<sub>3</sub> in BuOH at 100° 2 hrs. gave MeCH(OBu)<sub>2</sub> and a yellow polymer composed of 18% low mol. wt. material (mol. wt. av. 692) and 74% high mol. wt. material (av. 2112). The av. mol. wt. of the product can be controlled to some extent by addn. of BuOH in the course of polymerization for the purpose of chain-breaking. A reaction of 1 mole BuOCH<sub>2</sub>CH<sub>3</sub> and 0.5 mole BuOH yielded in addition to MeCH(OBu)<sub>2</sub> and the polymer, a small amt. of MeCH(OBu)CH<sub>2</sub>CH(OBu), b.p. 137-8°; n<sub>D</sub><sup>20</sup> 1.4259, d<sub>40</sub><sup>20</sup> 0.8661, which was also readily prep'd. by the reaction of BuOCH<sub>2</sub>CH<sub>3</sub> with MeCH(OBu)<sub>2</sub> in BuOH in the presence of FeCl<sub>3</sub> at 48-50°. G. M. Kosolapoff

SHOSTAKOVSKIY, M. F.

USSR

Chemical transformations of unsaturated and high-molecular compounds. II. Copolymerization of methyl ester of methacrylic acid with vinyl alkyl ethers. M. I. Shostakovskiy and A. M. Khomutov. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1954, 411-16 (Engl. translation).—See C.A. 48, 14201a. H. L. H.

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SHOSTAKOVSKIY, M. F.

✓ Transformations of vinyl aryl ethers. I. Ionic polymerization of vinyl aryl ethers. A. V. Bogdanova and M. R. Shostakovskii. *Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci.*, 1954, 789-806 (Engl. translation). II. Radical polymerization and copolymerization of vinyl aryl ethers. M. F. Shostakovskii and A. V. Bogdanova. *Ibid.* 797-801. — See *Ca. 49, 1861a*. B. M. R.

SHOSTAKOVSKIY, M. F.

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January

CH ✓ Chemical transformations of unsaturated an high molec-  
ular weight compounds. III. Copolymerization of methyl  
acrylic acid and its methyl ester with vinyl phenyl ether.  
M. P. Shostakovskii and A. M. Khomitov. *Bull. Acad.  
Sci. U.S.S.R., Div. Chem. Sci.* 1954, 803-70  
(See C.A. 49, 13021b.)  
B. M. P.

SHOSTAKOVSKIY, M. F.

Derivatives of unsaturated tertiary alcohols. II. Synthesis of methyl, ethyl, isopropyl, and butyl dimethyl(vinyl)carbinyl acetals. M. F. Shostakovskii and I. A. Shikhiev. Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1954, 809-12 [Engl. translation]. III. Synthesis of dimethyl(ethynyl) and vinylcarbinyl and methylethyl(ethynyl and vinyl)carbinyl *tert*-butyl acetals. M. F. Shostakovskii, I. A. Shikhiev, and V. I. Belyacy. Ibid. 821-4.—See C.A. 49, 13890d.

SHOSTAKOVSKIY, M.F.

Transformations of vinyl aryl ethers. I. Ionic polymerization of vinyl aryl ethers. A. V. Bogdanova and M. R. Shostakovskiy (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.R., Otdel. Nauk. Nauk. 1954, 9(1)-18.* — PhOCH<sub>2</sub>:CH<sub>3</sub> (10 g.) and 0.15 g. catalyst (TeCl<sub>3</sub>, AlCl<sub>3</sub>, or BF<sub>3</sub>OEt<sub>2</sub> in Et<sub>2</sub>O) were refluxed in dioxane, or 0.5 ml. 10% BF<sub>3</sub>OEt<sub>2</sub> in Et<sub>2</sub>O were refluxed in amyls at 13–18°; increase of viscosity became rapidly apparent (most rapid with BF<sub>3</sub>); similar results are obtained after 1–2.5 hrs. refluxing. The resulting polymers had low, mol. wt. (383–365), and were very viscous liquids, except for the one prep'd. with AlCl<sub>3</sub> catalyst in which case the polymer m. 40–50°, and had mol. wt. 405. Prepn. of the polymer with BF<sub>3</sub> catalyst at reflux under 2.6 mm. pressure gave the only colorless polymer. Fractionation of the crude products resulted in isolation of: diphenyl acetate and a solid fragile product, m. 45–7°, corresponding to (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>CH<sub>2</sub>. Mol. distn. gave a viscous (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>CH<sub>2</sub> with solid (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>CH<sub>2</sub>, m. 45–50°.  $\beta$ -Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>3</sub> with TeCl<sub>3</sub> catalyst gave 92% light-colored solid, m. 42–5°, corresponding to (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>CH<sub>2</sub>; similar to that obtained with BF<sub>3</sub> catalyst at room temp. With BF<sub>3</sub> catalyst at reflux under vacuum there was formed 86.7% solid polymer, m. 40–1°, corresponding to (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>CH<sub>2</sub>. Radical polymerization and copolymerization of vinyl aryl ethers. M. K. Shostakovskiy and A. V. Bogdanova. *Ibid.* 919–23. — The use of [CMes(CN)]N<sub>3</sub> as catalyst has resulted in successful polymerization of ArOCH<sub>2</sub>:CH<sub>3</sub>, as well as in their copolymerization. PhOCH<sub>2</sub>:CH<sub>3</sub> in 100 hrs. with 5% catalyst at 75° gave 21.6% volatile polymer, which yielded on fractionation a solid product, m. 44–5°, corresponding to (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub> and one, m. 44–5°, corresponding to (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>. Similarly,  $\beta$ -Ad<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>3</sub> gave 17.0% polymer, m. 48–5°, corresponding to (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>. A catalyst, (1:1) of PhOCH<sub>2</sub>:CH<sub>3</sub> and  $\beta$ -OCH<sub>2</sub>CH<sub>3</sub>, with 2% catalyst, gave 9.7% copolymer contg. 80.5% PhOCH<sub>2</sub>CH<sub>3</sub> units. With PhOCH<sub>2</sub>CH<sub>2</sub>-BtOCH<sub>2</sub>:CH<sub>3</sub>, the product (3.3%) contained 71.05% PhOCH<sub>2</sub>CH<sub>2</sub> units, while BtOCH<sub>2</sub>:CH<sub>3</sub>-MeCC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>3</sub> gave an 11.2% yield of product contg. 73% ArOCH<sub>2</sub>CH<sub>3</sub> units. The usual method mechanism with Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-indium iodide is proposed. G. M. P. -

SHOSTAKOVSKI, M. F.

✓ Chemical transformations of unsaturated and high molecular weight compounds. III. Copolymerization of methacrylic acid and its methyl ester with vinyl phenyl ether. M. F. Shostakovskii and A. M. Khomutov (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R.; Moscow). *Izvest. Akad. Nauk S.S.R., Otdel. Khim. Nauk* 1954, 6(24-30); cf. C.A. 49, 9061a.—Copolymerization of PhOCH<sub>2</sub>CH<sub>3</sub> with CH<sub>2</sub>:CMeCO<sub>2</sub>H (I) and its Me ester (II) were run at 60° in the presence of 0.2% Bz<sub>2</sub>O; a 1:1 ratio of the ether and II gave a copolymer sol. in 1:1 BuOH-PhOCH<sub>2</sub>CH<sub>3</sub>. At 1/4 ratio of II and PhOCH<sub>2</sub>CH<sub>3</sub>, the copolymer was formed similarly and its solv. was similar to the above. As the proportion of PhOCH<sub>2</sub>CH<sub>3</sub> in the initial mixt. was raised from 23% to 75%, the content of PhOCH<sub>2</sub>CH<sub>3</sub> units in the copolymer rose from 11.5 to 34.6%, but the yield of the copolymer declined from 76% to 10.66%. The abs. viscosity of the product declined from 0.021 to 0.0031, and relative viscosity from 3.89 to 1.09. Interaction of I and PhOCH<sub>2</sub>CH<sub>3</sub> in 3/1 ratio gave a 10% yield of product, contg. 57.88% I units. At 1:1 proportion of reactants, the product contained 42% I units and had mol. wt. 2206, while at 1:3 reactant proportion the product contained 53.5% I units. The liquid residue contained appreciable smts. of CH<sub>2</sub>:CMeCO<sub>2</sub>CHMeOPh. The results indicate that along with copolymerization side reactions take place which result in formation of acylals. G. M. Kosolapoff

SHOSTAKOVSKIY, M-F.

IV Derivatives of unsaturated tertiary alcohols. II. Synthesis of methyl, ethyl, isopropyl, and butyl dimethylvinyl acetals. M. F. Shostakovskii and I. A. Shil'chikov (N. D. Zelinskii Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow). *Invest. Akad. Nauk S.S.R., Otdel. Khim. Nauk* 1954, 931-5; cf. *C.A.* 48, 2307f.—To 21.5 g.  $\text{Me}_2\text{C}(\text{OH})\text{CH}=\text{CH}_2$  and 18 g.  $\text{MeOCH}=\text{CH}_2$  was added at  $-12^\circ$  0.016 ml. 30% HCl and the mixt. heated in sealed tube 9.5 hrs. at  $85^\circ$  to give after neutralization with  $\text{K}_2\text{CO}_3$  78%  $\text{MeOCHMeOCMeCH}=\text{CH}_2$ ,  $\text{b}_{11-12} 28-9^\circ$ ,  $\text{b}_{12-13} 192-3^\circ$ ,  $n_D^{20} 1.4130$ ,  $d_4^{20} 0.8601$ . Letting 43 g.  $\text{Me}_2\text{C}(\text{OH})\text{CH}=\text{CH}_2$  and 36 g.  $\text{EtOCH}=\text{CH}_2$  stand overnight with 0.013 ml. 30% HCl similarly gave 82.82%  $\text{EtOCHMeOCMeCH}=\text{CH}_2$ ,  $\text{b}_{11-12} 40-1^\circ$ ,  $\text{b}_{12} 146-7^\circ$ ,  $n_D^{20} 1.4118$ ,  $d_4^{20} 0.8502$ . Similarly were prep'd. 79% iso- $\text{POCHMeOCMeCH}=\text{CH}_2$ ,  $\text{b}_{11-12} 45-6^\circ$ ,  $\text{b}_{12} 166-7^\circ$ ,  $n_D^{20} 1.4126$ ,  $d_4^{20} 0.8422$ , and 80.8%  $\text{BuOCHMeOCMeCH}=\text{CH}_2$ ,  $\text{b}_{11-12} 182-3^\circ$ ,  $d_4^{20} 0.8390$ ,  $n_D^{20} 1.4148$ . III. Synthesis of dimethylethyne(vinyl) and methylethyne(vinyl) tert-butyl acetals. M. F. Shostakovskii, I. A. Shil'chikov, and V. I. Belyayev. *Ibid.* 945-8; cf. *C.A.* 49, 8111s.—Addn. of 0.02 ml. 30% HCl to 24.5 g.  $\text{MeEtC}(\text{OH})\text{C}=\text{CH}$  and 25 g.  $\text{Me}_2\text{COCH}=\text{CH}_2$ , followed by 5 min. at  $70-5^\circ$  and 12 hrs. at room temp. gave 60.6%  $\text{Me}_2\text{COCHMeOCMeEtCH}=\text{CH}_2$ ,  $\text{b}_{11} 88-9^\circ$ ,  $d_4^{20} 0.8694$ ,  $n_D^{20} 1.4290$ . Similarly were prep'd. 72.5%  $\text{Me}_2\text{COCHMeOCMe}_2\text{C}=\text{CH}_2$ ,  $\text{b}_{11} 68-9^\circ$ ,  $d_4^{20} 0.8692$ ,  $n_D^{20} 1.4204$ ; 81%  $\text{Me}_2\text{COCHMeOCMe}_2\text{CH}=\text{CH}_2$ ,  $\text{b}_{11} 55^\circ$ ,  $d_4^{20} 0.8532$ ,  $n_D^{20} 1.4250$ ; 74%  $\text{Me}_2\text{COCHMeOCMe}_2\text{EtCH}=\text{CH}_2$ ,  $\text{b}_{11} 70-81^\circ$ ,  $d_4^{20} 0.8540$ ,  $n_D^{20} 1.4250$ . The ethyryl derivs. are relatively less stable than their vinyl analogs; the former yellow in storage.

G. M. Kosolapoff

SHOSTAKOVSKIY, M.F.; PRILEZHAYEVA, Ye.N.; SHAPIRO, E.S.

Synthesis of sulfurous substances based on vinyl esters and acetylene. Report no.8. General method for the synthesis of  $\beta$ -alkoxyethyl-mercaptans. Izv. AN SSSR. Otd.khim.nauk no.2:303-313 Mr-Apr '54.  
(MIRA 7:6)

1. Institut organicheskoy khimii im. N.D.Zelinskogo Akademii nauk  
SSSR.  
(Mercaptans)

USSR/Chemistry Copolymerization

Card : 1/1

Authors : Shostakovskiy, M. F., and Khomutov, A. N.

Title : Study of chemical conversions of unsaturated and high-molecular compounds.  
Part 2.- Copolymerization of methyl methacrylate and vinyl alkyl ethers

Periodical : Izv. AN SSSR, Otd. Khim. Nauk., 3, 484 - 490, May - June 1954

Abstract : The copolymerization of methyl acrylate and vinyl alkyl ethers was investigated at different ratios under the effect of benzoyl peroxide. The copolymeric products obtained are described. Benzoyl peroxide promotes the copolymerization of vinyl alkyl ethers with compounds containing multiple C = C = O bonds. The reason for not finding methyl methacrylate polymers during the polymerization under the effect of benzoyl peroxide is explained. Sixteen references: 11 USSR; 1 German, 4 USA. Tables.

Institution : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Organic Chemistry

Submitted : March 20, 1953

*SHOSTAKOVSKY, M.F.*

USSR/Chemistry Quantitative analysis

Card : 1/1

Authors : Shostakovskiy, N. F., and Prilezhaova, E. N.

Title : Synthesis of sulfurous compounds on acetylene and vinyl ether bases.  
Part 9.- Synthesis and certain properties of beta-alkoxyethylvinyl sulfides

Periodical : Izv. AN SSSR, Otd. Khim. Nauk. 3, 517 - 525, May - June 1954

Abstract : A method for the synthesis of beta-alkoxyethylvinyl sulfides from beta-alkoxy methyl mercaptanes is described. A newly introduced method for quantitative determination of thiovinylic ethers, based on their decomposition reaction in the presence of mercuric chloride, is analyzed. A study of the chemical properties of beta-alkoxyethylvinyl sulfides showed that the reactions of thiovinylic ethers are much different than the reaction of their oxygen analogues. Sixteen references: 11 USSR, 4 USA and 1 German. Tables.

Institution : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Org. Chemistry

Submitted : Feb 10, 1953

*Shostakovskiy. M.F.*

USSR/Chemistry      Sulfurous compounds

Card            : 1/1

Authors        : Shostakovskiy, M. F., Prilezhaeva, E. N., and Uvarova, N. I.

Title          : Synthesis of sulfurous compounds on the vinyl ether and acetylene basis.  
Part 10.- Synthesis and certain conversions of vinylethyl sulfide.

Periodical     : Izv. AN'SSSR, Otd. Khim. Nauk. 3, 526 - 534, May - June 1954

Abstract       : Conditions favorable for the synthesis of vinylethyl sulfide with a yield of 60%, were established. The addition of mercaptan and hydrogen sulfide to vinylethyl sulfide when exposed to air, and the polymerization of the latter in the presence of  $FeCl_3$  and  $SnCl_2$  ion catalysts, are analyzed. The formation of mercurated ethylmercaptan salt was determined during the reaction of vinylethyl sulfide with mercuric chloride in alcohol and water solutions. The formation of an unstable complex salt, decomposing in water or alcohol, was established during the reaction in an ether solution. Twenty-two references: 10 USSR, 6 German, 4 USA. Tables.

Institution     : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Org. Chemistry

Submitted       : February 10, 1953

SHOSTAKOVSKIY, M. F.

Reactions between vinyl and polyfunctional compounds. II.  
Reaction of simple vinyl ethers with polyvinyl alcohol. M. F.  
Shostakovskii, V. V. Zhebrovskii, and M. A. Medelyadovskaya  
(*Izvest. Akad. Nauk SSSR, Otdel. khim. Nauk*, 1954, No. 3, 535—

540).—Vinyl butyl and vinyl phenyl ethers react with polyvinyl  
alcohol to produce polyacetals of polyvinyl alcohol. The reaction  
mechanism is discussed.

R. C. MURRAY.

SHOSTAKOVSKIY, M. F.

## USSR/ Chemistry      Synthesis

Card : 1/1      Pub. 40 - 15/27

Authors : Shostakovskiy, M. F., and Bogdanova, A. V.

Title : Investigation of acetylene alcohols and glycols. Part 3.- Multistage synthesis of acetals of acetylene glycals

Periodical : Izv. AN SSSR. Otd. khim. nauk 4, 677 - 682, July - August 1954

Abstract : Experimental data are presented showing the multistage mechanism of the formation of diacetals of acetylene glycals. The two basic methods - catalytic and thermal - by which multistage synthesis of diacetals is realized, are described. Symmetrization, which intensifies with the increase of molecular weights of the radicals of the basic vinyl ethers, was observed during the derivation of mixed diacetals from homologous monocetals. It was established that symmetrical diacetal is a product of substitution of the low-molecular alkoxy group by a high-molecular group. Seventeen references: 12 USSR; 3 French; 1 USA and 1 German (1912 - 1954). Tables.

Institution : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Organic Chemistry

Submitted : September 21, 1953

SHOSTAKOVSKIY, M. F.

## USSR/ Chemistry Reaction processes

Card : 1/1 Pub. 40 - 16/27

Authors : Shostakovskiy, M. F., Zhebrovskiy, V. V., and Madelyanovskaya, M. A.

Title : Investigation of reactions of vinyl and polyfunctional compounds. Part  
3.- Reaction of trivinylglycerin ether with ethylene glycol and 1,4-  
butylene glycol

Periodical : Izv. AN SSSR. Otd. khim. nauk 4, 683 - 688, July - August 1954

Abstract : The reaction process, in the case when both components (trivinylglycerin ether - ethylene- and 1,4-butylene glycols) are polyfunctional compounds was investigated. The ratio of the basic reaction components was found to be of great importance in the yield of reaction products. A vinyl ether surplus, which has the same effect as the reverse order of adding reagents, leads to displacement of the reaction toward cyclization of the monoacetal. The formation of cyclic acetals of glycols and glycerin is explained by the tautomerism of the acetals. Eight references:  
6 USSR; 1 USA and 1 German (1890 - 1954).

Institution : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Organic Chemistry

Submitted : May 20, 1953

SHOSTAKOVSKIY, M. F.

USSR/ Chemistry Hydrolysis

Card : 1/1 Pub. 40 - 17/27

Authors : Shostakovskiy, M. F., Sidel'kovskaya, F. P., and Zelenskaya, M. G.

Title : Ion hydrolysis of vinyl lactams in an acid medium

Periodical : Izv. AN SSSR. Otd. khim. nauk 4, 689 - 693, July - August 1954

Abstract : Ion hydrolysis of vinyl caprolactam and vinylpyrrolidone, was investigated under the effect of sulfuric acid. Lactams and acetaldehyde were found to be the products of ion hydrolysis. A method of quantitative determination of vinyl caprolactam and vinyl pyrrolidone, is described. The effect of acid concentration and temperature on the percentage yield of the hydrolysis products, is explained. Seven references: 6 USSR and 1 German (1900 - 1953). Tables.

Institution : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Organic Chemistry

Submitted : May 8, 1953

SHOSTAKOVSKIY, M. F.

USSR/Organic Chemistry - Synthetic Organic Chemistry, E-2

Abst Journal: Referat Zhur - Khimiya, No 19, 1956, 61593

Author: Shostakovskiy, M. F., Shikhiyev, I. A.

Institution: None

Title: Investigations of the Syntheses and Conversions of Organosilicon Compounds. Communication I. Synthesis of the Vinyl Ether of  $\gamma$ -hydroxypropyltrimethylsilane

Original  
Periodical: Izv. AN SSSR, otd. khim. n., 1954, No 4, 745-747

Abstract: Using  $\gamma$ -hydroxypropyl trimethylsilane (I) as an example the possibility has been ascertained of vinylating organosilicon alcohols. I was prepared by passing for 2.5 hours gaseous ethylene oxide (2 mol) into a cooled to -6° Grignard reagent (from 1 g-atom Mg in 800 ml absolute ether and 1 mol  $\alpha$ -chloromethyl trimethylsilane), yield 77.3%, BP 62-63°/10 mm  $n^{20}_{D}$  1.4298,  $d_4^{20}$  0.8408. The vinyl ether of  $\gamma$ -hydroxypropyl trimethylsilane  $CH_2=CH-OCH_2CH_2Si(CH_3)_3$  (II) obtained on heating in autoclave (8 hours, 180°) a reaction

Card 1/2

USSR/Organic Chemistry - Synthetic Organic Chemistry, E-2

Abst Journal: Referat Zhur - Khimiya, No 19, 1956, 61593

Abstract: mixture consisting of 20 g I, 2 g KOH and 60 g absolute dioxane,  
saturated with C<sub>2</sub>H<sub>2</sub> (18-20 atm, 20°), yield of II 35%, BP 60°/18  
mm, n<sup>20</sup>D 1.4286, d<sub>4</sub><sup>20</sup> 0.8168

Card 2/2

SHOSTUKOVSKIY, M. F.

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3041\* Investigation in the Field of the Conversion of  
Vinylaryl Esters. Issledovaniye v oblasti prevrashcheniya vinyl-  
arylykh estrov. II. Radical Polymerization and Copoly-  
merization of Vinylaryl Esters. Radiikal'naya polimerizatsiya  
i sopolimerizatsiya vinilarilovykh estrov. (Russian.) M. F.  
Shostukovskii and A. V. Bogdanova. Izvestia Akademii Nauk  
SSSR. Otdelenie Khimicheskikh Nauk, 1954, no. 5, Sept.-Oct.,  
p. 910-923.  
Includes tables, 7 ref.

*SHOSTAKOVSKIY, M.F.*

SHOSTAKOVSKIY, M.F.; SHIKHIYEV, I.A.; BELYAYEV, V.I.

Investigation in the field of derivatives of tertiary unsaturated alcohols. Report no.3. Synthesis of dimethylacetylenyl(vinyl)- and methylethylacetylenyl(vinyl)-tert-butyl acetals. Izv. AN SSSR Otd.khim. nauk no.5:945-948 S-O '54. (MLRA 8:3)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(Acetals)

Shostakovskiy, M. F.  
USSR/Chemistry - Analytical chemistry

Card 1/2      Pub. 40 - 22/27

Authors : Shostakovskiy, M. F.; Batuyev, M. I.; Tyupayev, P. V.; and Matveyeva, A. D.

Title : The oxonium theory and the optical study of the hydrogen bond in some monovinyl ethers of glycols and polyglycols

Periodical : Izv. AN SSSR. Otd. khim. nauk 6, 1103-1110, Nov-Dec 1954

Abstract : An optical study was conducted on several monovinyl ethers of liquid glycols and poly glycols to determine whether the valence of the oxygen in these compounds is variable and whether the intermolecular hydrogen bond is stable. The existence of the intermolecular hydrogen bond was also confirmed by other physico-chemical investigations.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Institute of Organ. Chemistry

Submitted : September 10, 1953

Periodical : Izv. AN SSSR. Otd. khim. nauk 6, 1103-1110, Nov-Dec 1954  
Card 2/2 Pub. 40 - 22/27

Abstract : The presence of the intermolecular hydrogen bond explained by the "abnormality" of the valence of the oxygen atom in the investigated ethers (its oxonium nature), and the chemical properties of these ethers. Eight USSR references (1940-1953). Table; graphs.

SHOSTAKOVSKIY, M. F.

USSR/ Chemistry - Synthesis

Card 1/2      Pub. 40 - 23/27

Authors : Shostakovskiy, M. F., and Chekulayeva, I. A.

Title : Synthesis and conversions of vinyl ethers of ethanol amines. Part 5

Periodical : Izv. AN SSSR. Otd. khim. nauk 6, 1111-1118, Nov-Dec 1954

Abstract : The processes occurring during the vinylation of di-and triethanol amines were investigated. It was found that the vinylation of above mentioned amines leads to the synthesis of complete and incomplete vinyl ethers. Experiments showed that vinyl ethers of diethanol amine and beta-aminoethanol do not submit to cyclization during the synthesis.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Institute of Org. Chemistry

Submitted : December 23, 1953

Periodical : Izv. AN SSSR. Otd. khim. nauk 6, 1111-1118, Nov-Dec 1954

Card 2/2 Pub. 40 - 23/27

Abstract : Certain chemical conversions of vinyl ethers of di- and triethanol amines were studies and their structure were analyzed. The vinyl ethers in ion conversions were seen to be less reactive than non-substituted vinylalkyl ethers. The tendency of the ethers toward polymerization is explained. Ten references: 7 USSR, 2 USA and 1 German (1931-1954). Tables.

Shostakovskiy, M. F.

USSR/Chemistry - Synthesis

Card 1/1 Pub. 40 - 25/27

Authors : Shostakovskiy, M. F.; Kochkin, D. A.; and Vlasov, V. M.

Title : Synthesis and conversions of oxygen-containing silicon-organic compounds

Periodical : Izv. AN SSSR. Otd. khim. nauk 6, 1120-1123, Nov-Dec 1954

Abstract : An investigation was conducted to determine the reaction between ethylene oxide and trialkyl(aryl)silane chlorides : trimethyl-, dimethylethyl-, tri-ethyl- and diethylphenylsilane chlorides. The derivation of 2-chloroethoxy dimethyl-, methyldiethyl- triethyl- and diethylphenylsilanes and their chemical characteristics are described. A new method for the derivation of oxygen-containing silicon-organic compounds is described. Five references: 3 USSR and 2 USA ( 1941-1954 ). Table.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Institute of Organ. Chemistry

Submitted : July 12, 1954

SHOSTAKOVSKY, M.F.

2446. Methods of analysis of halogenated ethers.  
II. Analysis of  $\alpha\beta$ -dihalogeno- and  $\alpha\beta\beta$ -trihalogeno-alkyl ethers. M. F. Shostakovskiy and S. P. Sidelnikovskaya. *J. Russ. Chem. U.S.S.R.* 1954,

9 [2], 105-108).—Dichloro- and trichloroethyl alkyl ethers are hydrolysed by water alone giving HCl, which can be titrated with alkali or with AgNO<sub>3</sub>.

G. S. SURIN

MF

SHOSTAKOVSKIY, M.F., professor; KONONOV, N.F.

Acetic acid manufacture. Khim.v shkole 9 no.6:15-23 N-D '54.  
(Acetic acid) (MLRA 8:1)

SHOSTAKOVSKIY, M. F.

3

USSR.

✓ Methods of analysis of simple halogenized ethers. II.  
Analysis of  $\alpha,\beta$ -dihalo and  $\alpha,\beta,\beta$ -trihalocalkyl ethers. M. F.  
Shostakovskii and N. P. Sidel'kovskaya. *J. Anal. Chem.*  
*U.S.S.R.* 9, 117-20 (1954) (Engl. translation).—See *C.A.* 48,  
6910e. H. L. H.

SHOSTAKOVSKIY, M.F.; SHIKHIYEV, I.A.; VLASOV, V.M.; BELYAYEV, V.I.

Synthesis of vinylisopropyl, vinyldibutyl and vinyldiamyl ethers  
and their conversions. Dokl. AN Azerb. SSR 10 no.7:473-482 '54.  
(MIRA 8:10)

1. Predstavleno deystvitel'nym chlenom Akademii nauk Azerbaydzhan-  
skoy SSR Yu.G.Mamedaliyevym.  
(Vinyl polymers)

SHOSTAKOVSKIY, M.F.; SHIKHIYEV, I.A.; RELYAYEV, V.I.

Investigation in the field of synthesis of derived tertiary unsaturated alcohols. Dokl. AN Azerb. SSR 10 no.11:759-765 '54.  
(MIRA 8:10)

1. Predstavлено деяствител'nym chlenom Akademii nauk Azerbay-dzhanskoy SSR Yu.G.Mamedaliyevym.  
(Alcohols)

SHOSTAKOVSKIY, M.F.

USSR/Chemistry - Physical chemistry

Card 1/1      Pub. 43 - 50/62

Authors : Kasatochkin, V. I.; Shostakovskiy, M. F.; Zil'herbrand, O. I.; and Kochkin, D. A.

Title : About hydrogen bonds in silanols

Periodical : Izv. AN SSSR. Ser. fiz. 18/6, 726-728, Nov-Dec 1954

Abstract : The infrared absorption spectra of trimethylcarbinol and five different silanols:  $(\text{CH}_3)_3\text{SiOH}$ ,  $(\text{CH}_3)_2\text{C}_2\text{H}_5\text{SiOH}$ ,  $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiOH}$ ,  $(\text{C}_2\text{H}_5)_3\text{SiOH}$  and  $\text{C}_6\text{H}_5(\text{C}_2\text{H}_5)_2\text{SiOH}$  were investigated in a range of wave lengths of from 2 - 4 to determine the nature of molecular association of silanols and the effect of the Si-atom on the hydroxyl group. It was established, among others, that the chem. properties of silanols, particularly their amphoteric properties, are due to the strengthening of the O-H bond and strong reaction between the oxygen and hydrogen of the neighboring molecules which takes place as result of increased polarity of the O-H bond. Graphs.

Institution : Acad. of Sc., USSR, Institute of Combustible Minerals

Submitted : .....

SHOSTAKOVSKIY, M. F.

"Investigations in the Field of Alcohol Oxides.II Preparation and Properties of  
a,B-Alcohol Oxides of the Aliphatic Series," Zhur. Obshch. Khim., 24, No.2, p.231, 1954

Comment B-87001, 27 Jul 55

SHOSTAKOVSKY, M. F.

3  
300

Synthesis of alkoxymethylprolactams. I. Alkoxymethylprolactams. M. F. Shostakovskij and F. P. Sidelkovskaya. *J. Gen. Chem. U.S.S.R.* 24, 1633-6 (1954). See C.A. #9, 130055. R. M. R.

(3)

AM 300

*SHOSTAKOVSKIY, M. F.*

USSR/Chemistry - Vinyl compounds

Card 1/1 : Pub. 151 - 19/42

Authors : Shostakovskiy, M. F., and Sidel'kovskaya, F. P.

Title : Synthesis of alkoxyethylidene lactams. Part 1.- Alkoxyethylidene caprolactams prolactams

Periodical : Zhur. ob. khim. 24/9, 1576-1581, Sep 1954

Abstract : The products obtained from the reaction of caprolactam with alpha-chloroethylbutyl and alpha-chlorodiethyl ether are described. It was found that the addition of caprolactam to vinyl butyl ether and butanol to vinyl-caprolactam, for the purpose of synthesizing butoxyethylidene caprolactam, brings unsatisfactory results especially with regard to the yield of the product searched for. The products formed during hydrolysis of alkoxyethylidene caprolactams in the presence of sulfuric acid are listed. Seven USSR references (1946-1954).

Institution : Acad. of Sc. USSR, Institute of Org. Chem., Laboratory of Vinyl Compounds

Submitted : May 10, 1954

SHOSTAKOVSKIY, M.F.

Oxygen-containing organosilicon compounds. III. Preparation of trimethyl- and triethylsilanols and their transformations. M. F. Shostakovskii, I. A. Shchukin, D. A. Kochkin, and V. I. Belyaev (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). Zhur. Obschestva Khim. 24, 2202-4 (1964); cf. C.A. 49, 1641b, 7610f. — Into 109 g.  $\text{Me}_3\text{SiCl}$  in dry  $\text{Et}_2\text{O}$  was passed dry  $\text{NH}_3$  9 hrs. at 0-7°. The ppptd.  $\text{NH}_3\text{Cl}$  was septd. and the soln. distd., yielding 64.2%  $\text{NH}(\text{SiMe}_3)_2$ , b.p. 125-130°, d<sub>4</sub><sup>20</sup> 0.7764, n<sub>D</sub><sup>20</sup> 1.4090. This (70 g.) was mixed with 25 ml.  $\text{H}_2\text{O}$ , 250 ml.  $\text{Et}_2\text{O}$ , and 10 drops methyl orange indicator soln., and treated with cooling to 0-7° with 250 ml. N HCl over 2.5 hrs. when the reaction was completed. Distn. of the org. layer gave 88.8%  $\text{Me}_3\text{SiOH}$ , b.p. 68-8.0°, d<sub>4</sub><sup>20</sup> 0.8130, n<sub>D</sub><sup>20</sup> 1.2802. This (22.5 g.), 21 g.  $\text{EtOCH}_2\text{CH}_3$ , and 0.004 g. HCl were heated in sealed ampul 8 hrs. at 65°, yielding 15.3%  $\text{MeCH}(\text{OEt})\text{OSiMe}_3$ , b.p.-n 38-9°, n<sub>D</sub><sup>20</sup> 1.3840, d<sub>4</sub><sup>20</sup> 0.8340, as well as 18.4 g.  $\text{O}(\text{SiMe}_3)_2$ , b. 90-100°, and 5.4 g.  $\text{MeCH}(\text{OEt})_2$ . Refluxing 151 g.  $\text{Et}_3\text{SiCl}$  with 102.1 g.  $\text{Ac}_2\text{O}$  5-6 hrs. with diahn. of  $\text{AcCl}$ , followed by slow addn. of the residue under the surface of 500 ml.  $\text{H}_2\text{O}$  and 20 ml. 18%  $\text{NH}_4\text{OH}$  below 6°, gave a top layer of  $\text{Et}_3\text{SiOH}$ , 75%, b.p. 80°, b.p. 153.5-4.5°, n<sub>D</sub><sup>20</sup> 1.4341, d<sub>4</sub><sup>20</sup> 0.8640; the same was formed in 91% yield when 100 g.  $\text{Et}_3\text{SiCl}$  in 500 ml. dry  $\text{Et}_2\text{O}$  and a few drops of phenolphthalein indicator were treated at -5 to +2° with N NaOH until a stable pink color formed; distn. of the org. layer gave the final product.  $\text{Et}_3\text{SiOH}$  has a camphor odor, is sparingly sol. in  $\text{H}_2\text{O}$ , can be stored in a well stoppered flask for long periods; on heating with mineral acids it is transformed to  $\text{O}(\text{SiEt}_3)_2$ ; it does not react with alkalies, but does react with Na and K on heating. Heating 33 g.  $\text{Et}_3\text{SiOH}$  and 21.5 g.  $\text{PrOCH}_2\text{CH}_3$  with 0.02 ml. HCl in ampul 10 hrs. at 65° gave 67.45%  $\text{MeCH}(\text{OPr})\text{OSiEt}_3$ , b.p.-n 80-90°, b.p. 204-5°, n<sub>D</sub><sup>20</sup> 1.4250, d<sub>4</sub><sup>20</sup> 0.8672. G. M. Kosolapoff

(3)

SHOSTAKOVSKIY, M.F.

ROZEN, B.Ya., kandidat khimicheskikh nauk (Leningrad)

Book about a famous Russian chemist ("Academician Aleksei Evgrafovich Favorskii. M.F.Shostakovskii. Reviewed by B.IA.Rozen). Priroda 43 no.8:122-124 Ag '54. (MIRA 7:8) (Favorskii, Aleksei Evgrafovich, 1860-1945) (Shostakovskii, M.F.)

SHOSTAKOVSKIY, M. F.

Chemical structure of acetals. M. F. Shostakovskii, M. I. Batuev, V. I. Belyaev, and A. D. Matveeva (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.R.* 94, 261-4 (1954).

In view of the known reactions of acetals (elimination of phenols on heating of aromatic-aliphatic acetals, disproportionation on heating of aliphatic acetals, alcoholytic reactions of aliphatic acetals) it was felt that their structures might involve tautomerism— with structures like  $\text{CH}_2:\text{CHOR} \cdots \text{HOR}$ . The following acetals were prep'd. for a test of this hypothesis; the syntheses were run by the reaction of  $\text{CH}_2:\text{CHOPh}$  with  $\text{MeCOH}$  or of guaiacol with  $\text{CH}_2:\text{CHOCMe}_2$  in the presence of a trace of  $\text{HCl}$ :  $\text{MeCH}(\text{OCMe}_2)\text{OPh}$ ,  $b_3$  83-4°,  $d_{25}^{\circ}$  0.9593,  $n_{D}^{20}$  1.4838;  $\text{MeCH}(\text{OCMe}_2)\text{OC}_6\text{H}_4\text{OMe}-o$ ,  $b_3$  111-12°,  $d_{25}^{\circ}$  1.0132,  $n_{D}^{20}$  1.4930. The intermediate  $\text{CH}_2:\text{CHOCMe}_2$ ,  $b_3$  75-52°,  $d_{25}^{\circ}$  0.7855,  $n_{D}^{20}$  1.3941. Raman spectra of the above acetals show many lines which exceed the sum of the lines caused by the phenol component as such and  $\text{Me}_2\text{COH}$  as such; in all instances the frequencies of these components are always present. This is believed to support the tautomerism suggested above. The double-bond line of  $\text{CH}_2:\text{CHOCMe}_2$  at 1637 cm.<sup>-1</sup> is weaker in the acetal than in the vinyl ether, as might be expected from the concept of tautomerism.

G. M. Kosolapoff

SHOSTAKOVSKY, M. F.

USSR

Chemical and physical properties of the hydroxyl group in trimethylsilanol. M. I. Batuev, M. F. Shostakovskii, V. I.

Belyayev, A. D. Matveeva, and E. V. Dubrova (N.D.

Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow).

Doklady Akad. Nauk S.S.R. 95, 531-4 (1954). —  $\text{Me}_3\text{SiOH}$ ,

m.  $-4.5^\circ$ , b.p.  $98-8.2^\circ$ , n<sub>D</sub><sup>20</sup> 1.3892, n<sub>D</sub><sup>25</sup> 1.3871, d<sub>4</sub> 0.8146, d<sub>2</sub>

0.8085, maintains its H-bond formation ability in soln., as

shown by cryoscopic detns.; in CCl<sub>4</sub> it forms assoc. com-

plexes with a rapid rise of apparent mol. wt. with the concn.

(shown graphically) to over that of a dimeric structure.

Hence in the pure liquid more complex structures can be

postulated. In the liquid state the Raman spectrum is

given. Me<sub>3</sub>COH also shows a wide HO band caused by H-

bonding. However, the fine structure in the Si deriv. indicates a greater acidic nature of the HO in the Si deriv. than

in the C analog. Me<sub>3</sub>SiOH reacts more vigorously with Na

and K at 0-3° than does the carbinol. Me<sub>3</sub>SiOH also forms

a ppt. of Me<sub>3</sub>SiONa with concd. NaOH. With traces of

acid catalyst Me<sub>3</sub>SiOH adds to vinyl ethers, forming acetals

(cf. Shostakovskii, *et al.*, *C.A.* 49, 1542a). However, Me<sub>3</sub>

SiOH also displays basic properties of the HO group, par-

ticularly shown by the Raman lines 3632 and 3702 cm.<sup>-1</sup>; in

CCl<sub>4</sub> the characteristic HO band vanishes and only the 3702

line remains; this must be due to the vibration of the

unassoc'd. HO group. It is shifted in respect to that of C

analog because of the electronegativity difference of Si.

G. M. K.

SHOSTAKOVSKIY, M. F.

## U S S R .

Oxygen-containing organosilicon compounds. Preparation of diethylphenylchlorosilane, diethylphenylsilanol, tetraethylidiphenyldisiloxane, and some of their transformations. M. F. Shostakovskii and D. A. Kochkin (N. D. Zelinskii Inst. Org. Chem., Acad. Sci., U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.R.* 95, 821-4 (1954). *Et<sub>2</sub>SiCl*, (157 g.) with either PhMgBr or PhLi (from 157 g. PhBr) in Et<sub>2</sub>O gave 60% *Et<sub>2</sub>PhSiCl*, *b*<sub>1</sub> 228°, *n*<sub>D</sub><sup>20</sup> 1.5130, *d*<sub>40</sub> 1.0252. When this (100 g.) in 500 ml. Et<sub>2</sub>O with a little phenolphthalein was treated with *N* NaOH until the pink color persisted, the org. layer and Et<sub>2</sub>O ext. of the aq. layer gave 91% *Et<sub>2</sub>PhSiOH*, *b*<sub>1</sub> 107.5-10°, *n*<sub>D</sub><sup>20</sup> 1.5170, *d*<sub>40</sub> 0.9905. Refluxed 2-3 hrs. with a few drops concd. HCl, this gave (*Et<sub>2</sub>PhSi*)<sub>2</sub>O, *b*<sub>1</sub> 210-18°, *n*<sub>D</sub><sup>20</sup> 1.5214, *d*<sub>40</sub> 0.9823. Heating 11 g. BuOCH<sub>2</sub>CH<sub>2</sub> and 9 g. *Et<sub>2</sub>PhSiOH* with 0.02 ml. H<sub>2</sub>SO<sub>4</sub> 1-1.5 hrs. on a steam bath gave after neutralization with K<sub>2</sub>CO<sub>3</sub> a no. of fractions which yielded 54.5% *Et<sub>2</sub>PhSiOCHMeOBu*, *b*<sub>1</sub> 120-3°, *n*<sub>D</sub><sup>20</sup> 1.4776, *d*<sub>40</sub> 0.9377.

SHOSTAKOVSKIY, M. F.

USSR

Synthesis and transformations of vinyl ethers of higher polyatomic alcohols and cellulose. Tetravinyl ether of  $\text{Me}\alpha\text{-glucoside}$ . M. F. Shostakovskii, E. N. Pylezheva, and L. V. Tsybul' (N.D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.R.* 95, 99-102 (1954).—Almost no vinylation of  $\text{Me}\alpha\text{-glucoside}$  takes place in the reaction with  $\text{C}_2\text{H}_4$  below 125°; above 160° colored products form; from several such runs there was obtained a small amount of a blue substance, b.p. 133-5°,  $n_{D}^{20}$  1.4920,  $d_{4}^{20}$  1.1037, which appeared to be  $\text{C}_4\text{H}_7\text{O}_4\cdot\text{C}_2\text{H}_4$ . Probably the best vinylation technique was as follows: 60 g.  $\text{Me}\alpha\text{-glucoside}$ , 12 g. KOH and 350 ml. dioxane was sated. with  $\text{C}_2\text{H}_4$  in an autoclave at room temp., then heated 11 hrs. to 125-45° with 133 g.  $\text{C}_2\text{H}_4$  being added to the app. Distn. of the product gave 84.8% tetravinyl ether of methyl glucoside, b.p. 138-40°, after redistn. from Na, the product b.p. 138-8.5°, m. 43-6°,  $[\alpha]_D^{20}$  146.3° ( $\text{CCl}_4$ ),  $n_{D}^{20}$  1.4820,  $d_{4}^{20}$  1.1029, it supercools easily. Shaking the product with 3.5% HCl gave AcH and methyl glucoside in 1.4 Lrs. at room temp.

G. M. Koslapoff

*SHOSTAKOVSKY*

*2 m/e*

Polymerization of vinyl compounds. I. Stepwise synthesis of polyvinyl buty ether. M. F. Shostakovskii and V. A. Gladyshevskaya (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow), Russ. Akad. Nauk S.S.R., Otdel. Khim. Nauk, 1955, 140-6; Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1955, 121-5; cf. 49, 4509a. -- A synthesis of products of progressively higher complexity and chain length in the formation of polymer of  $\text{BuOCH}_2\text{CH}_2$  was achieved. To 174 g.  $\text{MeCH(OBu)}_2$  was added 4 g. 5%  $\text{PcCl}_3$  in  $\text{BuOH}$  and the mixt., at 48-50°, was treated with 50 g.  $\text{BuOCH}_2\text{CH}_2$ , dropwise while maintaining a temp. of 60°; after 1 hr. at 50° the catalyst was pndtd. with powd.  $\text{Na}_2\text{CO}_3$ , the mixt. stirred 3 hrs., filtered and distd., yielding 82.3 g.  $\text{MeCH(OBu)}\text{CH}_2\text{CH(OBu)}_2$  (I),  $b_g$  131-5°,  $d_{42}^{20}$  0.8055,  $n_D^{20}$  1.4955 (viscosity 3.573 centipoises at 20°), and some 6.5 g.  $\text{MeCH(OBu)}\text{CH}_2\text{CH(OBu)}\text{CH}_2\text{CH(OBu)}_2$  (II),  $b_g$  175-7°,  $d_{42}^{20}$  0.8880,  $n_D^{20}$  1.4945. I and  $\text{BuOCH}_2\text{CH}_2$  treated similarly gave II and some  $\text{MeCH(OBu)}\text{CH}_2\text{CH}_2\text{CH(OBu)}\text{CH}_2\text{CH(OBu)}_2$  (III),  $b_g$  95-7°,  $d_{42}^{20}$  0.9033,  $n_D^{20}$  1.4135. II and  $\text{BuOCH}_2\text{CH}_2$  gave III and a residue of higher undistillable products. I, II and III are readily hydrolyzed in aq. medium in the presence of  $\text{NaHSO}_4$ .  
G. M. Kosolapov

*SHOSTAKOVSKIY, M.F.*

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Synthesis of sulfur compounds based on vinyl ethers and acetylene. XI. Ionic transformations of vinyl ethyl sulfide. M. F. Shostakovskii, E. N. Prilezheva, and N. I. Uvnova (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.R. Otdel. Khim. Nauk* 1955, 154-63; *Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci.* 1955, 136-41; cf. *C.A.* 49, 9483a.—Heating EtSCH<sub>2</sub>:CH<sub>3</sub> with 0.5*N* NH<sub>4</sub>OH-HCl 2 hrs. at 30° gave but 3.9-4.1% hydrolysis (estd. by titration of liberated HCl); in 24 hrs. at 20-30° this reached 57-57%, while 0.5 hr. at 100° gave 71.4-72.8% hydrolysis. Hydrolysis with 5% HCl in aq. dioxane 6 hrs. at 100° gave 76% MeCH(SEt)<sub>2</sub>, *b*<sub>2</sub> 64-67, *n*<sub>D</sub><sup>20</sup> 1.5023. After 1 hr. of acid-catalyzed hydrolysis the results approx. a reaction: 2 EtSCH<sub>2</sub>:CH<sub>3</sub> + H<sub>2</sub>O → MeCHO + MeCH(SEt)<sub>2</sub>, although the latter is also hydrolyzed further to EtSH and AcH in an apparently reversible reaction, some 34-5% hydrolysis occurring in 11 hrs. at 100°. EtSCH<sub>2</sub>:CH<sub>3</sub> (6 g.) and 4.6 g. EtOH treated with SO<sub>3</sub> for 5 min. at -10° then kept 2.5 hrs. at 24° and left overnight, then heated 5 hrs. at 60°, gave 50% MeCH(SEt)<sub>2</sub>, MeCH(OEt)<sub>2</sub>, and EtOH. In a similar reaction, in which a small amt. of HCl in dioxane was added to the reac-

tion mixt. and the latter heated 1.5 hrs. at 55-60°, gave EtOH, MeCH(OEt)<sub>2</sub>, EtSH and a small amt. of MeCH(SEt)<sub>2</sub>Et, *b*<sub>2</sub> 66.5-7°, *n*<sub>D</sub><sup>20</sup> 1.4451, *d*<sub>20</sub> 1.0038. The yield of the latter declines to 10-11% if the catalyst is aq. 30% HCl in the presence of dioxane, while the use of MeCHBr-SEt as the catalyst gave also a 10% yield of the mixed acetal. MeCH(SEt)ORT (0.5 g.) and 4.8 g. EtOH treated 5 min. with SO<sub>3</sub> at 0° then heated 1.5 hrs. at 60-5° and kept 2 days, gave EtSH and some MeCH(OEt)<sub>2</sub>, along with unidentified products. Passage of dry HCl into EtSCH<sub>2</sub>:CH<sub>3</sub> at -10° gave 80.9% EtSCHClMe, *b*<sub>2</sub> 46-7°, *n*<sub>D</sub><sup>20</sup> 1.4705, *d*<sub>20</sub> 1.012, which treated with H<sub>2</sub>O hydrolyzed nearly completely in 15 min. to AcH and HCl and MeCH(SEt)<sub>2</sub>. Dry HBr and EtSCH<sub>2</sub>:CH<sub>3</sub> gave 77.1% EtSCHBrMe, *b*<sub>2</sub> 39-41.5°, *n*<sub>D</sub><sup>20</sup> 1.5130, *d*<sub>20</sub> 1.3677, which fumes in air and can be stored only in abs. Et<sub>2</sub>O. If the addn. of HBr is made in pentane in the presence of a little (:NCMe<sub>2</sub>CN)<sub>2</sub> under N<sub>2</sub> the reaction being completed by 2 hrs. at 60-70°, the same product forms in 79.6% yield. EtSCHBrMe reacts rapidly with H<sub>2</sub>O and in 15 min. yields nearly 100% HBr, AcH and MeCH(SEt)<sub>2</sub>.

G. M. Kesolapoff

SHOSTAKOVSKIY, M.-F.

**V** Optical study of some vinyl ethers of ethanolamines. M. F. Shostakovskii, M. I. Batuev, I. A. Chekulaeva, and A. D. Matveeva (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.R. Otdel. Khim. Nauk Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci.* 1955, 481-6 (Engl. translation), 844-50; cf. *C.A.* 49, 7388b.—The previously reported vinyl ethers of ethanolamine and its analogs display the Raman characteristics of intramol. H bonds; the chem. inertness of some compds. in this group is ascribed to H bonding. The region of diffuse Raman lines at 3150-3400 cm.<sup>-1</sup> includes the O—H—O, as well as N—H—O bonds. The following Raman spectra are reported: CH<sub>2</sub>CHOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, 169(2), 248(4b), 385(0), 324(2), 382(2), 404(1), 435(1), 498(4), 603(3), 644(0), 710(3), 821(5b), 204(4), 966(4), 990(4), 1084(2), 1099(3), 1113(3), 1157(1), 1179(2), 1209(2), 1324(10), 1364(2), 1407(2), 1481(8), 1617(8), 1637(7), 247(7), 2632(8b), 3018(3), 2217(0), 3283(1), 3293(1), 3324(8b), 3385(3b); (CH<sub>2</sub>CHOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NH, 171(2), 241(4b), 802(3), 809(3), 680(0), 745(0), 778(0), 826(5b), 892(3), 938(0), 972(3), 1001(2), 1032(3), 1087(2), 1102(2), 1149(3), 1203(3), 1263(3), 1322(10), 1364(0), 1389(1), 1413(2), 1468(3), 1617(8), 1642(7), 2842(2), 2876(7), 2939(8b), 3022(4),

3225(0), 3271(1), 3338(4b); CH<sub>2</sub>CHOCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CO<sub>2</sub>Me, 163(1), 168(1), 236(3b), 824(1), 386(1), 431(0), 468(0), 605(1b), 811(0b), 658(0b), 708(1), 768(1), 813(1), 838(0b), 903(2b), 935(0), 973(3), 991(3), 1029(0), 1069(0), 1104(1), 1152(1b), 1203(1b), 1321(10), 1322(1), 1419(1), 1403(8), 1619(6), 1637(8), 1660(2), 1698(1), 1737(4), 2880(8), 2042(10b), 2772(3), 3020(2), 3032(0), 3176(1), 3224(1), 3274(1), 3342(4b); PhNHCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>, 125(3), 178(1), 214(2), 233(2), 248(2), 414(4b), 490(1), 510(1), 631(1), 676(0), 696(1), 819(4), 946(0), 663(0), 752(4), 782(4), 816(5), 838(0), 882(5), 871(0), 916(1), 933(10), 1029(5), 1073(0), 1155(4), 1182(3), 1198(0), 1287(1), 1320(6), 1356(0), 1380(0), 1408(0), 1434(0), 1455(1), 1493(1), 1603(10), 1619(1), 1639(1), 2850(0), 2376(4), 2933(4), 2984(0), 3024(1), 3821(1), 3351(1), 3406(4b); HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, 171(1), 482(4), 522(2), 838(4), 874(5), 1034(3), 1065(4), 1083(5), 1118(4), 1173(2b), 1248(3b), 1298(5), 1313(5), 1358(4b), 1400(10), 1593(1b), 2707(3b), 2802(10), 2914(9), 2942(9), 3145(1), 3187(3), 6239(2), 3300(6b), 3364(3b), 3150-3400 (HO band).

G. M. Kosolapoff

SHOSTAKOVSKIY, M.F.

✓ Reactions of vinyl and polyfunctional compounds. VI.

Reaction of vinyl ethers with pentazerythritol. M. F.

Shostakovskii, A. S. Atavin, and V. V. Zhebrovskii (N. D.

Zelinskii Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow).

*Izvest. Akad. Nauk S.S.R., Otdel. Khim. Nauk* 1955,

630-43; *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1955,

477-80 (Engl. translation); cf. *C.A.* 50, 4708b.—Mixing

20 g.  $C(CH_3OH)_4$  (I), 76.3 g.  $BuOCH_2CH_3$ , and 6 drops HCl

gave an exothermic reaction which yielded  $EtOH$ ,  $MeCH(OEt)_2$ ,

much resin, and 13 g.  $MeCH(OCH_3)_2C(CH_3O)CH_2CH_3$  (II), m:

40° (from  $EtOH$ ), b<sub>2</sub> 100-10°. I with  $BuOCH_2CH_3$  gave similarly  $BuOH$ ,  $MeCH(OBu)_2$ , and II.

I (20 g.) and 70.4 ml.  $BuOCH_2CH_3$  with 15 drops HCl

gave  $BuOH$ ,  $MeCH(OBu)_2$ , and 21 g. II. G. M. K.

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SHOSTAKOVSKY, M. F.

✓Reactivity of vinyl compounds and its manifestation in  
mechanisms of polymerization reactions. M. V. Shostakov-  
skiy. Voprosy Khim. Kinetiki, Kataliz i Reaktsionnoj  
Sposobnosti, Akad. Nauk S.S.R., Oddel. Khim. Nauk  
1953, 703-809; cf. C.A. 48, 12455f. --Review of Ionic and  
radical addns. of vinyl compds. 20 references.  
G. M. Kosolapoff

SHOSTAKOVSKIY, M.-F.

*✓* Synthesis of sulfur compounds based on vinyl ethers and  
acetylene. XIII. General method of synthesis of thio-  
vinyl ethers. M. F. Shostakovskii, E. N. Prilezhaeva, and  
N. I. Uvarova. Bull. Acad. Sci. U.S.S.R., Div. Chem.  
Sci. 1955, 821-7 (Engl. translation).—See C.I. 30, 9278c.  
B. M. R.

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SHOSTAKOVSKIY, M. F.

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✓ Synthesis and transformations of vinyl ethers of ethanodiamines. VII. The vinyl ether of 2-(diphenylamino)ethanol.  
M. F. Shostakovskif and I. A. Chikulaeva. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1955, 829-33 (Engl. translation).—See C.A. 50, 9325c.

2 M A. Yoo

Scop

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SHOSTAKOVSKIY, M.-F.

✓Chemical transformations on unsaturated and high-molecular weight compounds. VI. Copolymerization of vinylcaprolactum and methyl methacrylate in the presence of benzoyl peroxide and the dinitrite of 2,2'-azodisobutyric acid. M. F. Shostakovskii, I. P. Sidel'kovskaya, and A. M. Khomutov, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1955, 836-40 (Engl. translation).—See C.A. 50, 0202a. B. M. R.

Chem

3 M. A. YOUTZ

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SHOSTAKOVSKIY, M. F.

*Chair* ✓ Synthesis and transformations of oxygen-containing  
organosilicon compounds. II. Reaction of diethyl- and  
diphenylsilanediols with vinyl ethers. M. F. Shostakovskii,  
D. A. Kochkin, and V. M. Rog. Bull. Acad. Sci.  
U.S.S.R., Div. Chem. Sci. 1955, 871-3 (Engl. translation).  
See C.A. 50, 1320d.

B. M. R.

M. A. YOUTZ

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*Chem*  
V Synthesis of sulfur compounds based on vinyl ethers and acrylene. XIII. A general method of synthesis of this vinyl ethers. M. F. Shostakovskii, B. N. Prilezheva, and N. I. Uvarova (N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk S.S.R., Otdel. Khim. Nauk 1955, 908-12; cf. C.A. 50, 7080f.—Bu<sub>3</sub>SH (106.5 g.), 180 g. dioxane, 12; and 13.2 g. KOH (20 mole-%) satd. with C<sub>2</sub>H<sub>2</sub> in an autoclave in the cold, an C<sub>2</sub>H<sub>2</sub> pressure of about 30 atm, then maintained 1 hr. at 70–90°, the mixt. dilid. with Et<sub>2</sub>O, washed with H<sub>2</sub>O, and the org. layer distd. gave a series of fractions from which were isolated 96 g. BuSCH<sub>2</sub>:CH<sub>3</sub>, b.p. 47.5–8.5°, n<sub>D</sub><sup>20</sup> 1.4722, d<sub>4</sub><sup>20</sup> 0.8693, and 7.5% (CH<sub>3</sub>SBu). The use of an aq. soln. in the reaction gave but 30% of the sulfide, while EtOH, MePh, or C<sub>2</sub>H<sub>2</sub> gave zero yields. Similarly were obtained the following RSCH<sub>2</sub>:CH<sub>3</sub> (R, % yield, b.p./mm., d<sub>4</sub><sup>20</sup>, and n<sub>D</sub><sup>20</sup> given): Pr, 60, 43.6%/50, 0.8723, 1.4734; Et, 81, 91.9–2.2°/760, 0.8767, 1.4756;

SYNTHESIS OF SULFUR

iso-Am, 85, 53.5-4.5°/17, 0.8615, 1.4704; PhCH<sub>3</sub>, 76.2, 90-90.5°/7, 1.0347, 1.6794; Ph, 71.6, 76.5°/4, 1.0417, 1.5888 (this is best run in BuOH 3 hrs. at 145-60°). The disulfides are best obtained by mixing the corresponding mercaptans and thio vinyl ethers in contact with air; the reaction, which commences in a few min., is exothermic and cooling to 20-5° is advised, after which the mixt. is kept overnight and is distd. Thus were obtained (% yield, b.p./mm.,  $\eta^{\text{D}}$ , and  $d_4^{25}$  given): EtOCH<sub>2</sub>CH<sub>2</sub>SBu, 100, 98.5°/3.5, 1.5013, 0.9530; (CH<sub>3</sub>SPh)<sub>2</sub>, 100, 67.5°, —, —; BuSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OBu, 90, 165°/4, 1.4900, 0.9600; (CH<sub>3</sub>SP<sub>2</sub>)<sub>2</sub>, —, 91-2.5°/3, 1.5046, 0.9565; (CH<sub>3</sub>SBu)<sub>2</sub>, —, 131-2°/6, 1.4967, 0.9355. The vinyl thio ethers are quantitatively cleaved by HgCl<sub>2</sub> in EtOH so that this reaction may be used for analytical titration of such compds., yielding RSHgCl, HCl, and MeCH(OEt)<sub>2</sub>.

G. M. Kosolapoff

SHOSTAKOVSKII, M. F.

✓ Synthesis and transformations of vinyl ethers of ethanolamines. VII. The vinyl ether of 2-(diphenylamino)-ethanol. M. F. Shostakovskii and I. A. Chekulava (N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk S.S.R. Oddel. Khim. Nauk 1955, 913-18; cf. C.A. 49, 16189i; 50, 1622f. Heating Ph<sub>2</sub>NH with ethylene oxide in an autoclave to 220-40° gave 60-5% Ph<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH (I), b.p. 183-9°, d<sub>4</sub><sup>20</sup> 1.121, n<sub>D</sub><sup>20</sup> 1.6210. This (73 g.), 8 g., 1 K. salt, 200 ml. C<sub>6</sub>H<sub>6</sub>, and 14-16 atm. C<sub>2</sub>H<sub>2</sub> gave, after 3 hrs. at 180°, 74.5% Ph<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OCH:CH<sub>2</sub>, b.p. 168-9°, n<sub>D</sub><sup>20</sup> 1.6980, d<sub>4</sub><sup>20</sup> 1.0698. In dioxan soln. the yield reaches 81.5%; the use of KOH catalyst gave 62-66.5% yields in C<sub>6</sub>H<sub>6</sub>. The ether hydrolyzes with 2% H<sub>2</sub>SO<sub>4</sub> at 95° to AcH and I. Hydrogenation of I over Raney Ni gave Ph<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OEt<sub>2</sub>, b.p. 158-9°, n<sub>D</sub><sup>20</sup> 1.5920, d<sub>4</sub><sup>20</sup> 1.0800. Ph<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OCH:CH<sub>2</sub> (8.7 g.) and 7.2 g. I treated with 1 drop concd. HCl and kept 4 hrs. after the exothermic reaction yielded 62.5% MeCH(OCH<sub>2</sub>CH<sub>2</sub>NPh<sub>2</sub>)<sub>2</sub> (II), b.p. 232-4°, n<sub>D</sub><sup>20</sup> 1.6185, d<sub>4</sub><sup>20</sup> 1.1176. Similarly the vinyl ether with BuOH gave MeCH(OBu)<sub>2</sub> and II, as well as a wide fraction of materials which decompr. during distn., yielding BuOCH:CH<sub>2</sub> and I. A similar reaction with MeOH gave II and MeCH(OMe)<sub>2</sub>, as well as decompn. products, including I. FeCl<sub>3</sub> (5% in BuOH) polymerizes Ph<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OCH:CH<sub>2</sub> to 29% of a viscous dark liquid, mol. wt. about 600; concd. HCl gives about 31% polymer, mol. wt. 420-60; (:NCMe<sub>2</sub>CN)<sub>n</sub> polymerizes the vinyl ether to a yellow oil, mol. wt. 475, in a very low yield after 100 hrs. at 60°. G. M. K.

SHOSTAKOVSKIY, M. F.

✓Chemical transformations on unsaturated and high-molecular weight compounds. VI. Copolymerization of vinyl-caprolactam and methyl methacrylate in the presence of benzoyl peroxide and the dinitrile of 2,2'-azodiisobutyric acid. M. F. Shostakovskii, F. P. Sidel'kovskaya, and A. M. Khadimov (N. D. Zelinskii Inst. Org. Chem., Moscow).

*Trans. Akad. Nauk S.S.R., Otdel. Khim. Nauk 1955, 919-21; cf. C.A. 47, 9917g; 48, 6159c; 50, 1674h.*—Vinylcaprolactam and  $\text{MeO}_2\text{CCMe}_2\text{CH}_2$  were copolymerized in the presence of either  $\text{Bz}_2\text{O}_2$  or ( $\text{:NCMe}_2\text{CN}$ )<sub>n</sub> in various proportions of the monomers. The content of methacrylate links in the copolymers ranged from 85.7 to 27.6 mole-%. The products were sol. in  $\text{Me}_2\text{CO}$ ,  $\text{C}_6\text{H}_6$ , and  $\text{EtOH}$  but insol. in  $\text{Et}_2\text{O}$ ; those with high content of methacrylates were insol. in  $\text{H}_2\text{O}$ . The polymerizations were run at 60° for 48-72 hrs. with 0.3% initiator. The copolymers appeared to be inhomogeneous in their behavior with solvents, but no polymers of the initial monomers alone were found.

G. M. Kosolapoff

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*Chase*

*M.F. 8/9/01*

SHOSTAKOVSKIY, M.-F.

Synthesis and transformations of oxygen-containing organosilicon compounds. II. Reaction of diethyl- and diphenylsilanediols with vinyl ethers. M. F. Shostakovskii, D. A. Kochkin, and V. M. Rog (N. D. Zelinskii Inst. Org. Chem., Moscow). Izv. Akad. Nauk S.S.R., Otdel. Khim. Nauk 1955, 953-5; cf. C.A. 50, 5550d.  $\text{Et}_2\text{Si}(\text{OH})_2$ , (12 g.) and 50 g.  $\text{BuOCH}=\text{CH}_2$  treated with 1 drop conc'd HCl and heated 1.5-2 hrs. at 60° yielded 37%  $\text{Et}_2\text{Si(OCH}_2\text{CH}_2)_2$ .  $\text{Mc}_2\text{Bu}_2$ , b.p. 137-9°, n<sub>D</sub><sup>20</sup> 1.1370, d<sub>4</sub><sup>20</sup> 0.9010, and a residue of polysiloxanes. The product treated with 5%  $\text{H}_2\text{SO}_4$  3-4 hrs. at 100° gave 95-98% AcH. Similar reaction of  $\text{Ph}_2\text{Si}(\text{OH})_2$  with  $\text{BuOCH}=\text{CH}_2$  gave  $\text{MeCH}(\text{C-Bu})_2$  and a high-boiling material from which it was impossible to isolate the expected silanoacetate  $\text{Ph}_2\text{Si(OCHMeOBu)}_2$ , owing to its thermal instability. Hydrolysis with dil. acid readily gave 82-83% AcH. G. M. Kosolapoff.

SHOSTAKOVSKY, M. F.

Polymerization of vinyl isopropyl and vinyl cyclohexyl ethers under the influence of isobutyro-2,2'-azobisisnitrile.  
M. F. Shostakovskii, F. P. Sidel'kovskaya, and E. S. Shishkina  
Zhur. Vsesoyuz. Inst. Org. Chern. M. Nauk. 1955, 1955, 1955.

In CH<sub>2</sub>Cl<sub>2</sub> at 40°C. wt. % 57% NC.  
In solvents, focus liquids, of unknown mol. wt. CH<sub>2</sub>Cl<sub>2</sub> under similar conditions gave polymers, m.w. up to 1440, the products contg. 57% NC. The polymers were sol. in usual solvents  
at 40°C. after 10-150 hrs. also gave polymeric or dimeric products, m.w. up to 2000, in 20% yield.

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*Shostakovskiy, M.F.*

## USSR/Chemistry - Conversions

Card 1/1 Pub. 40 - 16/27

Authors : Shostakovskiy, M. F., and Khomutov, A. M.Title : Study of chem. conversions of unsaturated and high-molecular compounds.  
Part 4. Copolymerization of certain vinyl compounds with monovinyl ether  
of ethylene glycol

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 126-132, Jan-Feb 1955

Abstract : The characteristics of copolymerization reactions of monovinyl ether of ethylene glycol with methacrylic acid, its methyl ether and styrene are explained. The synthesis of copolymers of methacrylic acid and its methyl ether with monovinyl ether of ethylene glycol is described. The effect of a monovinyl ether increase in the reaction medium on the yield of copolymers is discussed. It is shown that styrene monovinyl ether of ethylene glycol do not form copolymers in the presence of benzoyl peroxide. Nine Russian and USSR references (1869-1954). Tables.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Org. Chem.

Submitted : September 25, 1953

*Shostakovskiy, M. F.*

## USSR/Chemistry - Conversions

Card 1/2      Pub. 40 - 17/27

Authors : Shostakovskiy, M. F., and Khomutov, A. M.

Title : Chemical conversions of unsaturated and high-molecular compounds. Part 5.  
Copolymerization of methyl ether of acrylic acid and vinyl ethers

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 133-139, Jan-Feb 1955

Abstract : The conditions favorable for the copolymerization of methyl ether of acrylic acid (methyl acrylate) with vinyl ethyl, vinyl-n-butyl and vinyl phenyl ethers are described. It is shown that the composition of the copolymers depends largely upon the vinyl ether and methyl acrylate concentrations in the reaction mixture.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Org. Chem.

Submitted : December 23, 1953

Card 2/2

Pub. 40 - 17/27

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 133-139, Jan-Feb 1955

Abstract : Methyl acrylate and vinyl ether copolymers were found to possess a greater number of vinyl ether rings in their composition than the copolymers formed by methyl metacrylate and vinyl ethers. Nine references: 8 Russian and USSR and 1 USA (1869-1954). Tables

*Shostakowskij, M. F.*

USSR/Chemistry - Polymerization

Card 1/2            Pub. 40 - 18/27

Authors : Shostakovskij, M. F., and Gladyshevskaya, V. A.

Title : Polymerization of vinyl compounds. Part 1. Multistage synthesis of polyvinylbutyl ether.

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 140-145, Jan-Feb 1955

Abstract : Experimental data are presented regarding the multistage synthesis of individual products of various complexity and closely related to polyvinylbutyl ether. The distinguishable characteristics of chain free-radical and ion reactions, resulting in the formation of only high molecular compounds regardless of reaction time, are analyzed.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Org. Chem.

Submitted : December 23, 1953

Card 2/2

Pub. 40 - 18/27

Periodical :

Izv. AN SSSR. Otd. khim. nauk 1, 140-145, Jan-Feb 1955

Abstract :

It is pointed out that free-radical chain polymerization occurs as result of opening the double bonds and consequent addition of molecules. The mechanism of ion-chain polymerization of vinyl compounds is explained. Some products obtained from multistage synthesis are described. Ten references: 1 USA and 9 USSR (1935-1954). Table

*Shostakowsky, M. F.*

## USSR/Chemistry - Synthesis and conversion

Card 1/2 Pub. 40 - 19/27

Authors : Shostakovskiy, M. F., and Chekulayeva, I. A.

Title : Synthesis and conversions of vinyl ethers of ethanolamines. Part 6.  
Vinyl ether of beta-(phenylamino)ethanol

Periodical : Izv. AN SSSR. khim. nauk 1, 146-153, Jan-Feb 1955

Abstract : A study of chemical conversions of vinyl ether of beta-(phenylamino)ethanol showed that the compound investigated experiences a series of conversions when subjected to the effect of concentrated hydrochloric acid resulting in the formation of 2-methyl-3-phenylcycloisolidine, beta-(phenylamino)ethanol and a C<sub>12</sub>H<sub>15</sub>ON compound.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Organ. Chem.

Submitted : December 23, 1953

Card 2/2      Pub. 40 - 19/27

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 146-153, Jan-Feb 1955

Abstract : The results obtained from the vinylation of beta-(phenylamino)ethanol showed that this compound easily converts into cyclic acetal. Sixteen references: 12 USSR, 2 German and 2 USA (1901-1954). Tables

*Shostakovskiy, M. F.*

## USSR/ Chemistry - Synthesis and conversion

Card 1/2      Pub. 40 - 20/27

Authors : Shostakovskiy, M. F.; Prilezhayeva, Ye. N.; and Uvarova, N. I.

Title : Synthesis of sulfurous substances on the vinyl ether and acetylene basis.  
Part II. Ion conversions of vinylethyl sulfide

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 154-162, Jan-Feb 1955

Abstract : It is shown experimentally that ion reactions of vinylethyl sulfide with water, alcohol and halogen hydacid have a certain inherent specificity but by their general nature are closely analogous to vinyl allyl ethers. The conditions most favorable for the hydrolysis of vinylethyl sulfide were established, together with the conditions leading to the addition of

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Org. Chem.

Submitted : November 14, 1953

Card 2/2 Pub. 40 - 20/27

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 154-162, Jan-Feb 1955

Abstract : the alcohol to the vinyl ethyl sulfide and the formation of monothiacetal. The conditions most suitable for the hydrohalogenation of vinyl ethyl sulfide are described. Thirteen references: 8 USSR, 2 USA, 2 German and 1 Dutch (1889-1954). Tables